Synthesis of Alkylphosphoranes

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Abstract: The synthesis is described of the first stable pentaalkylphosphorane, **6**, and of some phenyl-substituted analogs (Scheme I). These phosphoranes are stable because strain in the precursory tetravalent phosphonium salt is relieved when a fifth substituent attaches to phosphorus. An alternative explanation, that the methyl protons in **8**, for example, are less acidic than those in tetramethylphosphonium iodide, is excluded by the observation that in 0.27 *N* NaOD at 26.8° the methyl protons in **8** exchange with deuterons 44 times faster than those in tetramethylphosphonium iodide. The latter explanation also does not account for the reactions shown in Scheme II, of phosphine oxide **9** with phenyllithium and HBr giving diphenylphosphonium salt **2** and of **10** with methyllithium giving **8**, while the former explanation does. Alkylphosphoranes in general should be preparable if two of the substituents are constrained in a ring that is sufficiently small. Whether a cyclic phosphonium salt reacts with an organolithium reagent to give an ylide or a pentasubstituted phosphorane should depend on the ring angle at the phosphorus, and, if so, the angle below which pentasubstituted phosphoranes form and above which ylides form is bracketed between that in the bicyclo[4.2.1]nonane and the bicyclo[2.2.1]heptane ring systems. Thus **24a** with phenyllithium gives the ylide **25**, while **20**, which differs from **24a** by only one bond, gives phosphorane **21** instead. In accord with these results is the failure to prepare the diphenylphosphonium salt **24a** from phosphine oxide **22**, phenyllithium, and HBr and the success of the analogous preparation of salt **20** from phosphine oxide **19**. The pentavalent phosphoranes fragment thermally as shown in eq 5 and 6 and at rates indicated in Table III. That phosphoranes **37** and **41** fragment at room temperature is shown by phosphonium salts **35** and **36** with organolithiums giving semibullvalene (**39**, Scheme VI) and by **40** with phenyllithium giving cyclooctatetraene (eq 4). Exposure to ultraviolet light converts phosphoranes **3** and **6** into *syn*-tricyclooctadiene (**43**). The pentavalent oxyphosphoranes that form when **33** and **49** react with phenyllithium or methyllithium (eq 7–10) fragment with skeletal rearrangement as indicated in Scheme VII and eq 11.

Pentamethylphosphorane has never been isolated. Although pentaphenylphosphorane is formed when tetraphenylphosphonium bromide reacts with phenyllithium[1] (eq 1), tetramethylphosphonium iodide with

$$(C_6H_5)_4\overset{+}{P}Br^- \xrightarrow{C_6H_5Li} (C_6H_5)_5P \qquad (1)$$

methyllithium gives the ylide instead (eq 2).[2] That

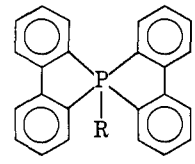
$$(CH_3)_4\overset{+}{P}\ I^- \xrightarrow{CH_3Li} \begin{cases} \not\rightarrow (CH_3)_5P \\ \rightarrow (CH_3)_3P{=}CH_2 + CH_4 \end{cases} \qquad (2)$$

pentasubstituted phosphoranes,[3] one of whose substituents is an alkyl group, are unstable is illustrated by the reaction (eq 3) of tetraphenylphosphonium bromide with methyllithium giving methylenetriphenylphosphorane, presumably through the intermediacy of methyltetraphenylphosphorane.[4,5] That alkylphosphonium salts and organolithium reagents in general give ylides is shown by the generality of Wittig's olefin synthesis.[6]

$$(C_6H_5)_4\overset{+}{P}Br^- \xrightarrow{CH_3Li} [(C_6H_5)_4PCH_3] \longrightarrow (C_6H_5)_3P{=}CH_2 + C_6H_6 \qquad (3)$$

However, as seen in Scheme I, diphenylphosphoniahomocubane bromide (**2**) with phenyllithium gives not the ylide, but the triphenylphosphorane **3**, a stable product.[7] There are two possible reasons. Either there must be a peculiar instability preventing formation of the ylide, or there must be a peculiar stability enhancing formation of the pentavalent phosphorane. A bridged ring system might prevent the ylide from forming by inhibiting the resonance stabilization of the anion, but it has not prevented the formation of some bridged sulfur ylides.[8] A bridged ring system might enhance formation of the pentavalent phosphorane by straining the internal angle at phosphorus in the tetracoordinate phosphonium salt, an effect analogous to that suggested to explain the quickened rate of hydrolysis of small-ring phosphate esters.[9]

That the latter explanation is correct is indicated by **4**, **5**, and **6** (Scheme I),[10] and the alkylbis(biphenylene)phosphoranes (**1**)[11] being stable isolable compounds,



1, R = alkyl

and by the effectiveness of a synthesis of angle-strained phosphonium salts from strained phosphine oxides.[7] **6** is the only stable pentaalkylphosphorane known. The synthesis of the homocubylphosphoranes was reported in preliminary communications;[7,10] details of their chemistry and extensions of this research to the

(1) G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 187 (1949).
(2) G. Wittig and M. Rieber, *ibid.*, **562**, 177 (1949).
(3) We use the term phosphorane to mean a compound with five carbon atoms bonded to phosphorus.
(4) D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Amer. Chem. Soc.*, **87**, 3467 (1965).
(5) Methyltriphenylphosphonium bromide with phenyllithium forms methyltetraphenylphosphorane reversibly prior to forming an ylide: D. Seyferth, W. B. Hughes, and J. K. Heeren, *ibid.*, **87**, 2847 (1965).
(6) (a) G. Wittig and G. Geissler, *Justus Liebigs Ann. Chem.*, **580**, 44 (1953); (b) A. Maercker, *Org. React.*, **14**, 270 (1965).
(7) T. J. Katz and E. W. Turnblom, *J. Amer. Chem. Soc.*, **92**, 6701 (1970).
(8) (a) W. von E. Doering and L. K. Levy, *ibid.*, **77**, 509 (1955); (b) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 417, 427 (1964).
(9) (a) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); (b) R. Kluger and F. H. Westheimer, *J. Amer. Chem. Soc.*, **91**, 4143 (1969).
(10) E. W. Turnblom and T. J. Katz, *ibid.*, **93**, 4065 (1971).
(11) D. Hellwinkel, *Chem. Ber.*, **98**, 576 (1965).

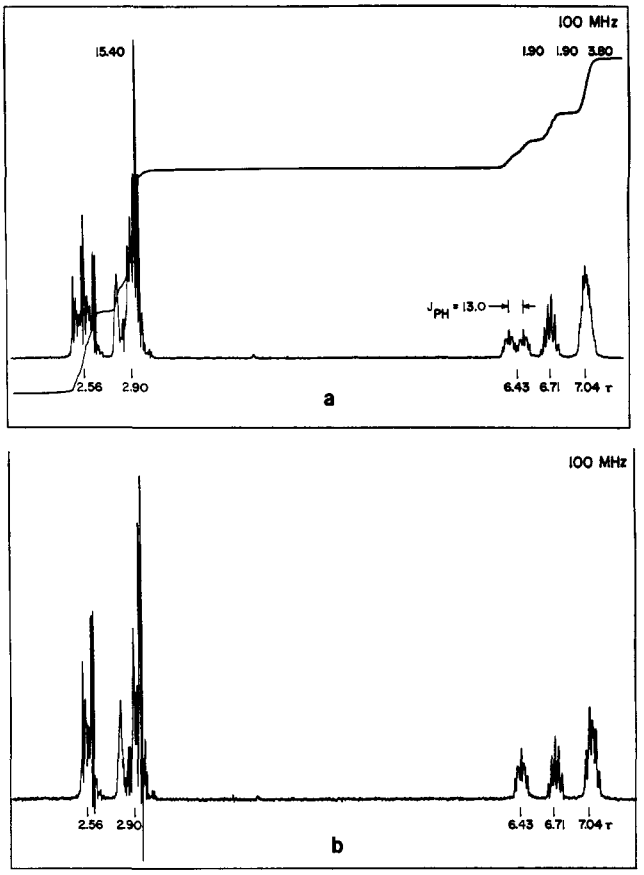


Figure 1. Proton nmr spectra of the homocubylphosphoranes in C_6D_6: (a) **3**; (b) **3**, ^{31}P irradiated.

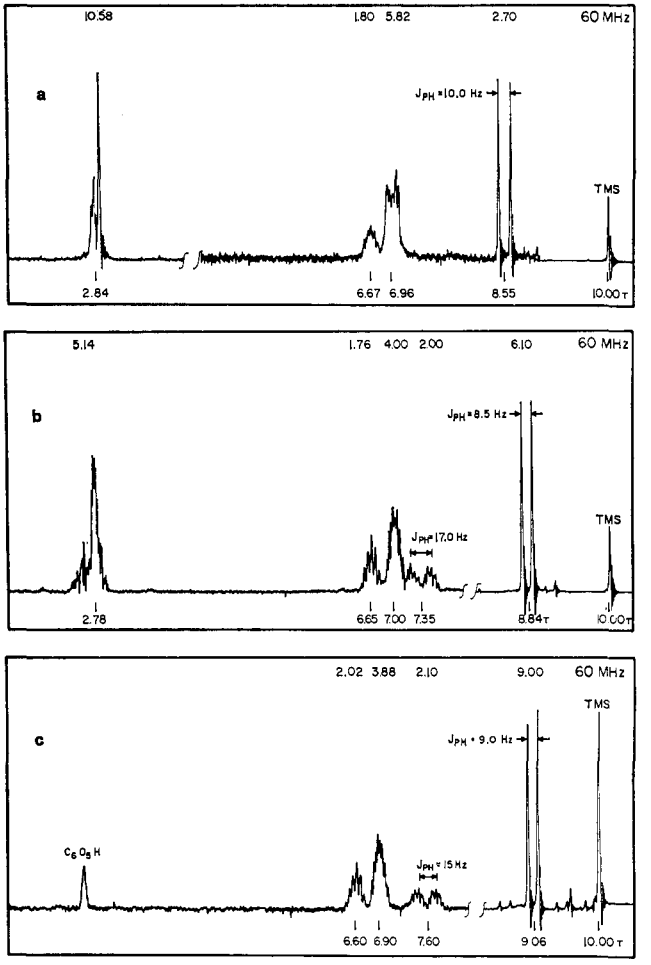


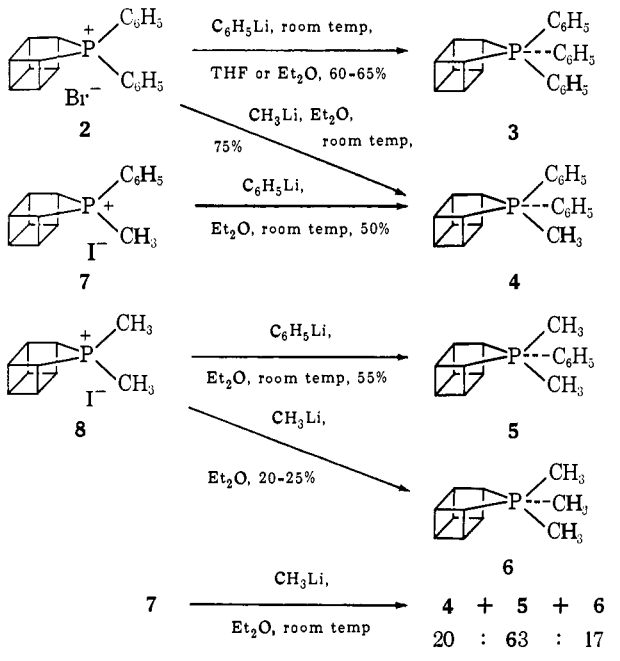
Figure 2. Proton nmr spectra of the homocubylphosphoranes in C_6D_6: (a) **4**; (b) **5**; (c) **6**. In spectrum a the amplification is increased above τ 4 and in spectrum b and c decreased above τ 8.

synthesis of phosphoranes of other ring systems are presented below.

Results

A. Synthesis of the Homocubylphosphoranes. The synthesis of the homocubylphosphoranes is summarized in Scheme I. The phosphonium salt **2** with phenyllithium in ether or tetrahydrofuran (THF) gives the triphenylphosphorane **3**; with methyllithium in ether it gives the diphenylmethylphosphorane **4**, which is also formed from the phenylmethyl salt **7** and phenyllithium but in lower yield. The dimethyl salt **8** with phenyllithium gives the dimethylphenylphosphorane **5** and with methyllithium the homocubyltrimethylphosphorane **6**. The phenylmethyl salt **7** with methyllithium does not give **5** cleanly; it gives a mixture of phosphoranes **4**, **5**, and **6** as shown in Scheme I.

Scheme I



The structures of the phosphoranes are assigned on the basis of their nmr spectra, shown in Figures 1 and 2 and analyzed in Table I, and their mass spectra. An X-ray crystallographic structure determination, which is in progress, confirms the structure of **3**.[12] **3** and **4** are crystalline, while **5** and **6** are liquids distillable at 10^{-6} mm.

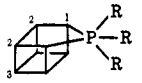
The salts were prepared as shown in Scheme II, **2** by reacting phosphine oxide **9**[13] with phenyllithium in THF at −78° and then aqueous HBr, and **7** and **8** by reducing phosphine oxides **9** and **10** with Si_2Cl_6[14] and then quaternizing with methyl iodide. Salt **8** could also be prepared from **10** with methyllithium

(12) J. Mayerle, Columbia University. We thank Dr. Mayerle for his results.

(13) T. J. Katz, J. C. Carnahan, Jr., G. M. Clarke, and N. Acton, *J. Amer. Chem. Soc.*, **92**, 734 (1970).

(14) K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 2788 (1969).

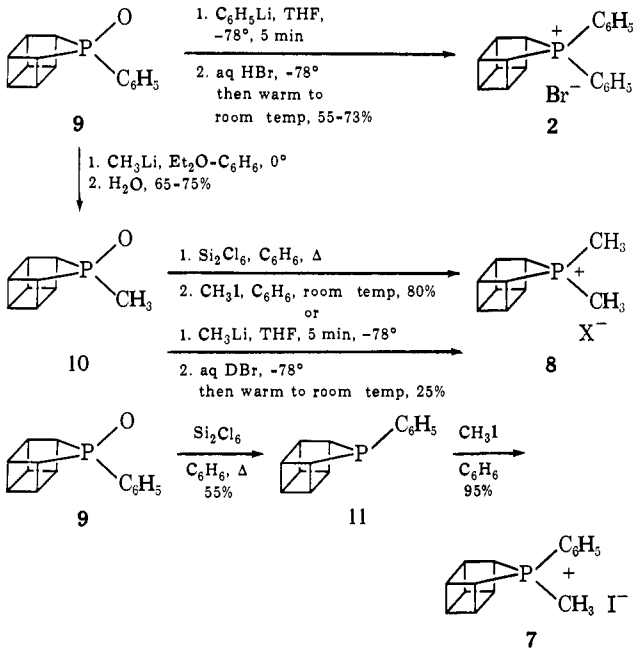
Table I. Proton Nmr Assignments of the Homocubylphosphoranes



Phosphorane	Chemical shifts (τ) H_1	H_2	H_3	R = C_6H_5	R = CH_3
3	6.43	7.04	6.71	2.56, 2.90	
4	6.96[a]	6.96	6.67	2.84	8.55
5	7.35	7.00	6.65	2.78	8.84
6	7.60	6.90	6.60		9.06

[a] This resonance, rather than that at 6.67, is assigned to H_1 because it, and not the other, is simplified when the ^{31}P nucleus is decoupled.

Scheme II

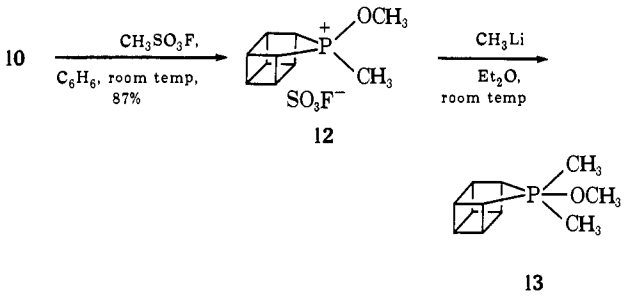


and DBr at −78°. Each salt was characterized by its nmr spectrum and elemental analyses.

Oxide **10** was prepared from **9** and methyllithium and was characterized by its nmr and mass spectra and by its elemental analyses. Phosphine oxide **9** and the corresponding phosphine **11** had been reported previously.[13]

While phenylphosphahomocubane oxide (**9**) in THF with phenyllithium at −78° and then HBr gives the diphenylphosphonium salt **2**, the reaction with phenyllithium at room temperature does not. The only product recovered is the starting material (**9**). If the reaction is quenched with D_2O the recovered **9** contains one deuterium atom on the caged-ring system (presumably adjacent to phosphorus; mass spectrometry and proton nmr analysis; see Experimental Section). Similarly, while oxide **10** with methyllithium in THF at −78° and DBr gives dimethyl salt **8**, at room temperature it does not; it gives back **10** containing deuterium in the methyl group (nmr analysis). When the reaction that gives **10**, that of **9** with 1 mol of methyllithium, is quenched with D_2O, the product (**10**) contains one deuterium on the methyl group.

An improved synthesis of **6** has been found since the first report of its preparation. In an attempt to prepare the methoxyphosphorane **13**, the methoxyphosphonium salt **12** was treated as shown below. Thus

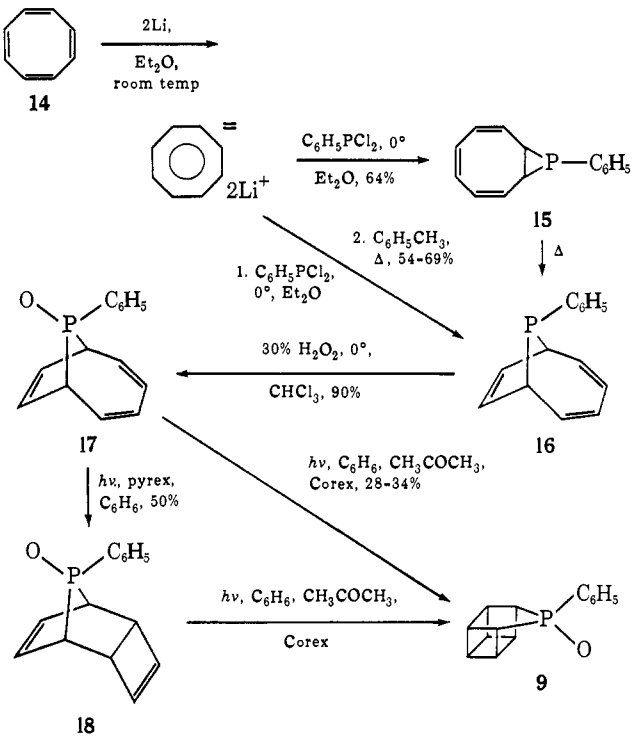


12 with 2 equiv of CH_3Li in ether at room temperature gives after quenching with water and extraction with ether the trimethylphosphorane **6** in 44.5% yield (based on **12**). This is the only product detectable by nmr. Extraction of the aqueous layer with chloroform gives oxide **10** in 48% yield. No **13** is revealed.[15,16]

Salt **12** was prepared from oxide **10** and methyl fluorosulfonate[17] in benzene. It is hygroscopic and was characterized only by its nmr spectrum; it was used unpurified in the next step.

The phosphine oxide **9** was prepared as shown in Scheme III using reactions previously described,[13,18]

Scheme III



but with three refinements that improve the yield. For the synthesis of **16**,[18] lithium was substituted for potas-

(15) Our phosphoranes are all soluble in ether, while our phosphonium salts (except **2**) and phosphine oxides are soluble in chloroform.

(16) An alternative route to **13** also failed. Thus **8** with sodium methoxide in methanol or ether gave only starting material on work-up with water; **8** with lithium methoxide in ether–THF, followed by removal of the solvents and direct nmr analysis, also showed no **13**.

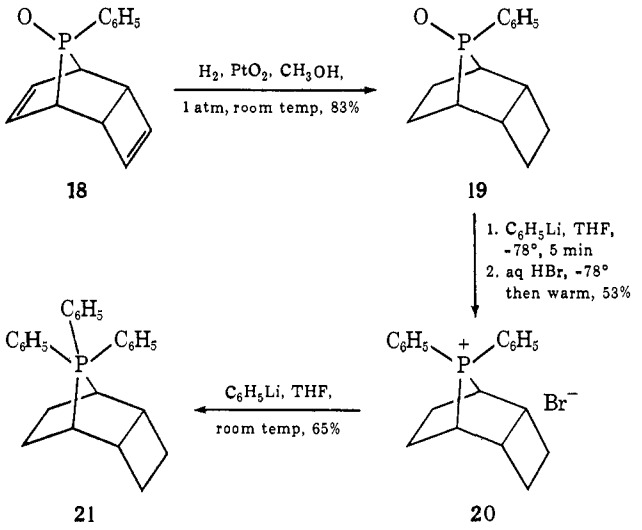
(17) Sulfoxides have been *O*-methylated with this reagent; see M. G. Ahmed, R. W. Alder, G. H. James, M. L. Sinnott, and M. C. Whiting, *Chem. Commun.*, 1533 (1968).

(18) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Amer. Chem. Soc.*, **88**, 3832 (1966).

sium and ether for THF. The initially formed product (**15**) was not isolated, but was rearranged thermally to **16** by warming it in toluene.[19] The yield of **16** from cyclooctatetraene **14** was then 54–69% after recrystallization.

The synthesis of **15** was also greatly improved, and it could be obtained in crystalline form in 64% yield as shown in Scheme III.

B. Other Ring Systems. The possibility that the bridged phosphorus compounds that are the precursors of **9** might also serve as precursors for the construction of other alkylphosphoranes was also studied. Hydrogenating the double bonds in **18** gives **19,** which with phenyllithium in THF and then aqueous HBr gives salt **20.** When this salt is combined with phenyllithium in THF it does indeed give the phosphorane **21,** a



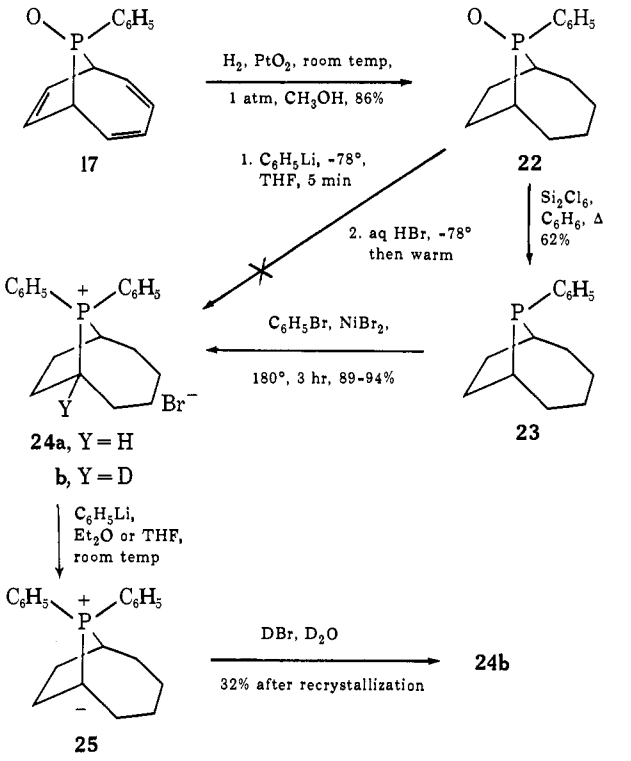
crystalline solid whose structure is shown by its proton nmr and mass spectra and by its elemental analyses.[20]

The phosphonium salt **24a**, whose skeleton differs from that of **20** by one bond, behaves differently. With phenyllithium (Scheme IV) it gives not a phosphorane, but instead the bridgehead phosphorus ylide, **25**,[20] as shown by the following. When the reaction mixture is quenched with 48% DBr in D_2O and extracted with ether, no pentavalent phosphorane or triphenylphosphine (an anticipated fragmentation product of the phosphorane) is found.[15] When the reaction mixture is extracted with chloroform, deuterated salt **24b** is the only product recovered.[15] Its nmr spectrum is identical with that of **24a**, except that the intensity of the bridgehead resonance at τ 5.25 is diminished. In three separate experiments, the intensity of this resonance is 0.89, 1.01, and 1.07, assuming the sum of the intensities of all the remaining resonances is 22.00.

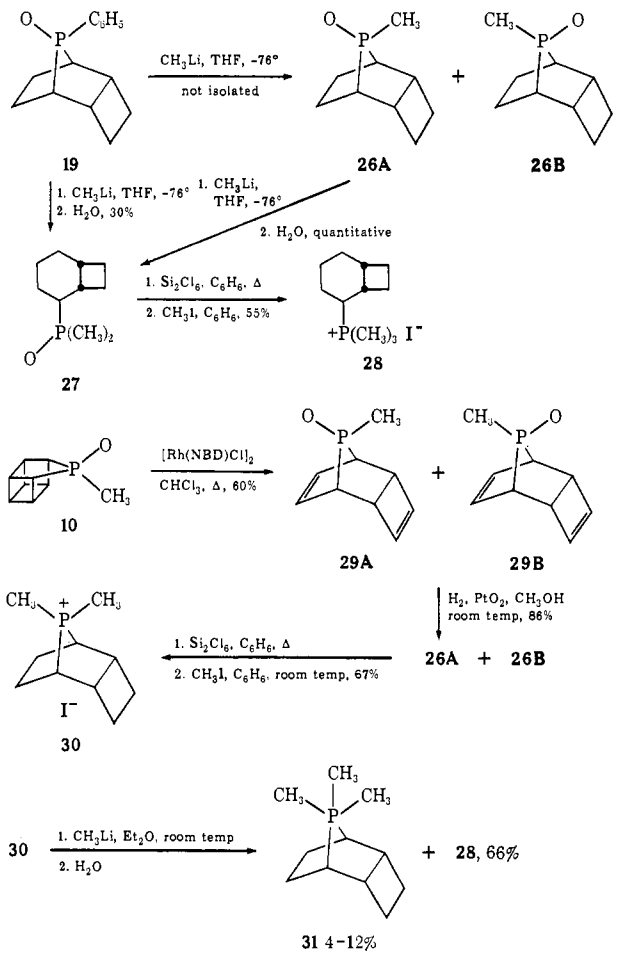
Salt **24a** could not be prepared by combining oxide **22** with phenyllithium and then aqueous HBr. That only **22** is recovered is shown by the nmr spectrum of the crude reaction mixture. The salt can be prepared as shown in Scheme IV by reducing oxide **22** to phosphine **23** and quaternizing with bromobenzene and $NiBr_2$.[21] It is hygroscopic and the material isolated from aqueous solutions gives off water when heated above 120°. Its structure is consistent with its proton nmr spectrum and its elemental analyses.

Oxide **22** was prepared by hydrogenating **17**; its

Scheme IV



Scheme V

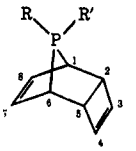


(19) These experiments were first performed by J. C. Carnahan, Jr.

(20) Preliminary communication: E. W. Turnblom and T. J. Katz, *J. Chem. Soc., Chem. Commun.*, 1270 (1972).

(21) *Cf.* L. Horner, G. Mummenthey, H. Moser, and P. Beck, *Chem. Ber.*, **99**, 2782 (1966).

Table II. Proton Nmr Chemical Shifts (τ), Intensities, and Coupling Constants (Absolute Values, Hz) of **18** and **29**



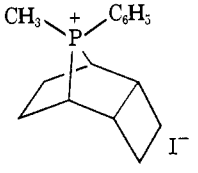
Proton	**18**,[a] R = O, R′ = C_6H_5	P epimer of **18**,[a] R = C_6H_5, R′ = O	**29A**,[b] R = O, R′ = CH_3	**29B**,[b] R = CH_3, R′ = O
$H_{1,6}$	6.77 (m, 2.04 H)	6.95 (m, 1.95 H)	7.17 (m, 1.99 H)[d]	7.17 (m, 1.99 H)[d]
$H_{2,5}$	7.10 (d, 1.95 H)	6.20 (d, 1.97 H)	6.83 (d, 1.17 H)[e]	6.32 (m, 0.82 H)[e]
	$J_{1,2}$ = 3.2	$J_{1,2}$ = 2.9	$J_{1,2}$ = 3.2	
$H_{3,4}$	4.50 (s, 1.90 H)	4.21 (s, $^1/_2$·3.92 H)[c]	4.32 (s, 1.96 H)[d]	4.23 (s, 1.96 H)[d]
$H_{7,8}$	3.73 (d of t, 1.97 H)	4.00 (d of t, $^1/_2$·3.92 H)[c]	3.72 (d of t, 1.96 H)[d]	3.92 (d of t, 1.96 H)[d]
	J_{PH} = 11.0	J_{PH} = 12.5	J_{PH} = 11.0	J_{PH} = 11.0
	$J_{6,7}$ = 3.2	$J_{6,7}$ = 3.5	$J_{6,7}$ = 3.0	$J_{6,7}$ = 3.0
Aromatics	2.65 (m, 5.14 H)	2.61 (m, 5.16 H)		
H_{P-CH_3}			8.40 (d, 3.10 H)[d]	8.40 (d, 3.10 H)[d]
			J_{PH} = 12.0	J_{PH} = 12.0

[a] Reference 13. [b] The nmr spectrum was determined at 60 MHz using a mixture of **29A** and **29B**. [c] The observed intensity is the sum of the intensities of the resonances overlapping at τ 4.00 and 4.21. [d] The resonances assigned to **29A** and **29B** overlap. This intensity is the sum of the intensities of resonances of the epimers. [e] These intensities indicate that the mixture consists of 59% of one epimer and 41% of the other. The assignments for **29A** and **29B** might be reversed. See Experimental Section.

structure is consistent with its nmr and mass spectra and its elemental analyses.

An attempt to prepare a second pentaalkylphosphorane by combining salt **30** with methyllithium is summarized in Scheme V. The attempt required that **30** be synthesized, and three syntheses were devised before one succeeded. Thus while **19** with 1 equiv of methyllithium might give **26**, the only product obtained when the reaction is performed in THF at −78° is **27**, isolated in 30% yield after purification. Compound **26** is probably an intermediate, and on reaction with methyllithium it (see below) does in fact give **27** quantitatively. The nmr spectrum of **27** is featureless except for a P–CH_3 doublet, but is consistent with the structure as there are no olefinic or aromatic resonances and the mass spectrum shows the molecular ion to be the required 186. The stereochemistry of the phosphorus–ring bond is not known.

An attempt to prepare **26** by hydrolyzing **32** (pre-



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pared from oxide **19** by reduction with Si_2Cl_6 and quaternization with methyl iodide) in aqueous alkali[22] gives a mixture of possibly four compounds (there are four P–CH_3 proton nmr resonances), which was not further characterized.

Finally, **26** and **30** were synthesized successfully as follows. Methylphosphahomocubane oxide (**10**) with $[Rh(NBD)Cl]_2$[23] in refluxing chloroform gives a mixture of epimers **29A** and **29B**. The structure of these epimers is shown by the mass spectrum of the mixture, which exhibits the required parent peak, and by the similarity, summarized in Table II, of their proton nmr spectra and those of **18** and its phosphorus epimer.[13] Hydrogenating **29A** and **29B** gives **26**, and reduction and quaternization then gives **30**. The structure of **30** is consistent with its nmr spectrum and its elemental analyses.

With methyllithium in ether, **30** gives, after quenching with water and extracting with ether,[15] a small amount (4–12% in eight experiments; the yield is not improved if the reaction is performed at −78°) of an oil, which is possibly the trimethylphosphorane **31**, but the compound is unstable and cannot be characterized fully. Its proton nmr spectrum shows a resonance attributable to P–CH_3 at τ 9.00, $|J|$ = 8.5 Hz, whose position and splitting is similar to that of the P–CH_3 resonance of **6** (*cf.* Figure 2c), but otherwise the spectrum is featureless. Neat samples or C_6D_6 solutions decompose completely in a few hours at room temperature; it can, however, be stored neat or in C_6D_6 at −78° for several weeks. The decomposition products could not be identified. A satisfactory mass spectrum could also not be obtained. The major product of the reaction is the phosphonium salt **28**, obtained in 66% yield by acidifying the aqueous layer (after extraction with ether) with HI and extracting with chloroform.[15] Salt **28** was prepared independently from oxide **27**; both samples had identical ir and nmr spectra.

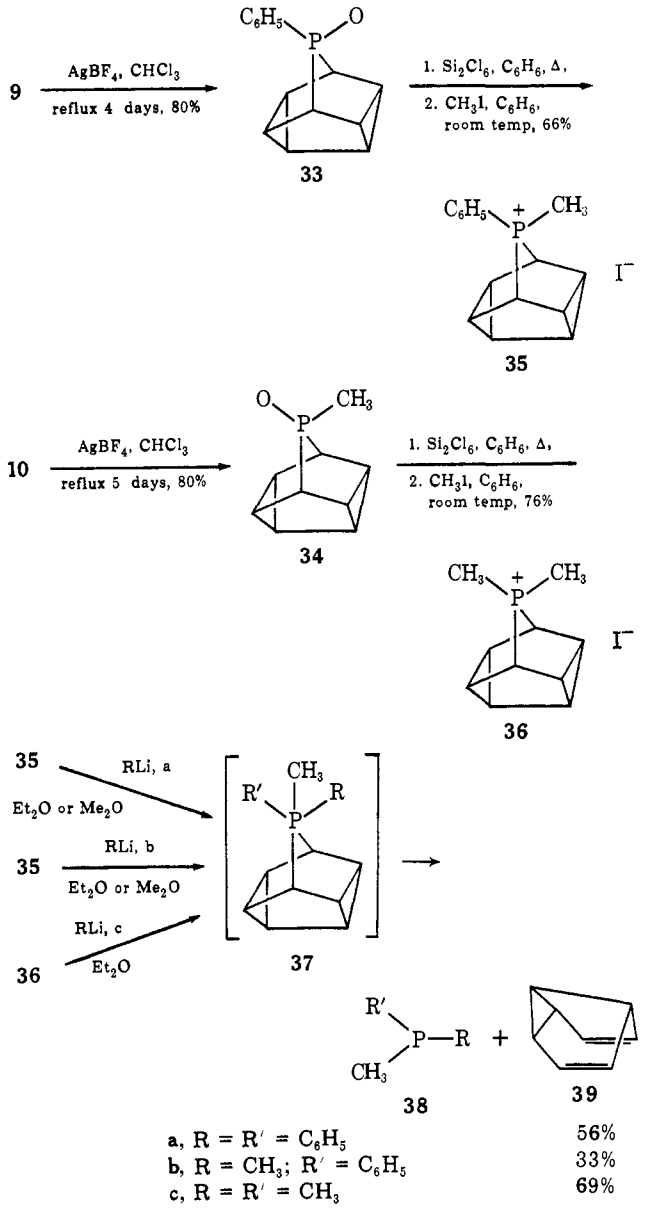
As shown in Scheme VI, the bridged phosphine oxides **33** and **34** can be prepared by isomerizing the phosphahomocubane oxides **9** and **10** by refluxing them in chloroform for 4–5 days with $AgBF_4$.[24] The oxides **33** and **34** were shown by mass spectroscopy to be isomeric with **9** and **10**, respectively, and their nmr spectra showed they were saturated and possessed a plane of symmetry. We assign their structures on the basis of these facts and precedent for this rearrangement among other cubanes.[24] The methiodides **35** and **36** can be prepared from these oxides as shown in the scheme, and their proton nmr spectra are acceptable. The phosphine oxide **33**, however, is not

(22) *Cf.* K. L. Marsi, F. B. Burns, and R. T. Clark, *J. Org. Chem.*, **37**, 238 (1972).

(23) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970).

(24) (a) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. Palmer, *Tetrahedron Lett.*, 787 (1970); (b) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2585 (1970).

Scheme VI

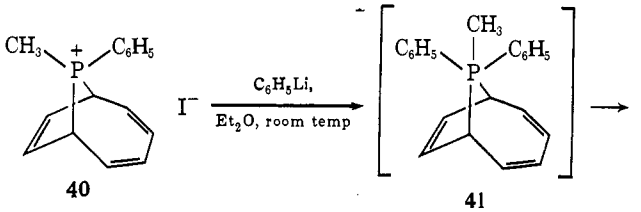


converted into the corresponding diphenylphosphonium salt with phenyllithium and HBr, nor is it converted into **34** with methyllithium. Skeletal rearrangements occur instead (see below).

Salt **35** with phenyllithium or methyllithium in ether gives no pentavalent phosphorane **37a** or **37b** after work-up with water and extraction with ether. Instead it gives semibullvalene (**39**) in 56% yield together with diphenylmethylphosphine (**38a**) when phenyllithium is the reagent, and in 33% yield together with dimethylphenylphosphine (**38b**) when methyllithium is the reagent. Similarly, salt **36** with methyllithium gives semibullvalene in 69% yield together with trimethylphosphine (**38c**). Using dimethyl ether rather than diethyl ether as the solvent facilitates the isolation of semibullvalene; the yield is not significantly different. Semibullvalene (**39**) was identified by its nmr and ir spectra,[25] phosphines **38a** and **38b** by the methyl doublets in their proton nmr spectra, and phosphine **38c**, after quaternization with methyl iodide, by its nmr.

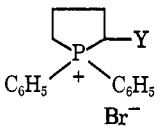
(25) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969).

Methiodide **40**[18] with phenyllithium[26] in ether gives diphenylmethylphosphine (identified by its P–CH_3 nmr doublet) and cyclooctatetraene (**14**), the latter in 31% yield (eq 4). The reaction is not clean and produces much polymeric material, but isolation of the fragmentation products implies that phosphorane **41** is an intermediate. If an ylide is also formed from **40**, it must be destroyed before work-up, for no **40** is recovered when the reaction mixture is quenched with aqueous HI.



14 + $(C_6H_5)_2PCH_3$ (4)

The simple phospholanium salt **42a**,[27] unlike **2** and **20** but like **24a**, gives no phosphorane after reaction with phenyllithium, quenching with 48% DBr in D_2O, and extraction with ether, but gives salt **42b** in 45% yield after extraction with chloroform.



42a, Y = H
b, Y = D

C. Deuterium Exchanges. The rate at which dimethylphosphoniahomocubane iodide (**8**), in 0.27 *N* NaOD at 26.8°, exchanges its methyl protons for deuterons was measured. The pseudo-first-order rate constant is $(5.84 \pm 0.22) \times 10^{-5}$ sec^{-1}, and assuming the reaction rate is proportional to the deuteroxide ion concentration,[28] the second-order rate constant is 2.16×10^{-4} l. mol^{-1} sec^{-1}. Per methyl this is 44 times the rate at which tetramethylphosphonium iodide exchanges under the same conditions.[28] The bridgehead protons in **8** also exchange, but more slowly. The rate was not measured accurately, but in 1 *N* LiOD at room temperature the methyl protons in **8** exchange in a few hours, while the bridgehead protons remain unaffected for 1 week. However, the latter also exchange when the temperature is raised to 100°. Thus the proton nmr intensity ratios measured for the resonances of the cage protons at τ 6.02 and 6.35, the bridgehead protons at 5.50, and the methyl protons at 7.75 were: after 13 hr at room temperature, 6.00:1.97:0.55; after 1 week at room temperature, 6.00:2.02:0.43; and after 6 days at 100°, 6.00:0.13:0.55. The salt was recovered after each exchange experiment in greater than 80% yield.

How rapidly diphenylphosphoniahomocubane bromide (**2**) exchanges its bridgehead protons for deuterons in 1 *N* LiOD in D_2O at 100° cannot, however, be determined because the salt hydrolyzes to the phosphine

(26) With methyllithium **40** gives no identifiable products.
(27) K. Issleib, K. Krech, and K. Gruber, *Chem. Ber.*, **96**, 2186 (1963).
(28) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 77, 521 (1955).

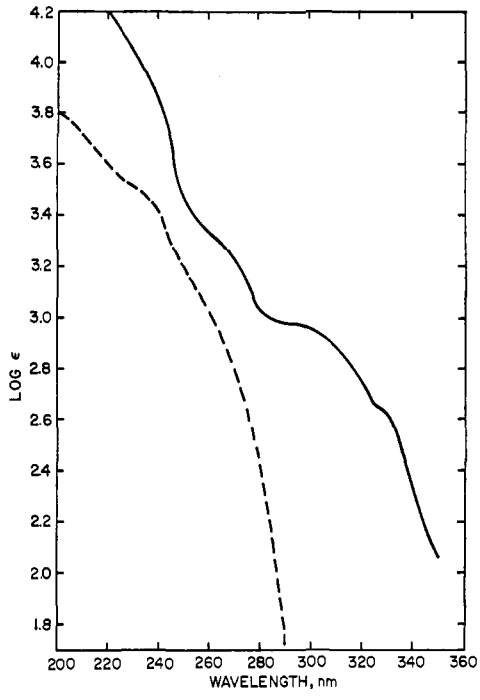


Figure 3. Ultraviolet spectra of **3** (———) and **6** (- - - - - -) in cyclohexane.

oxide **9** faster than any protons exchange. Thus after 20 hr the phosphine oxide **9** is isolated in slightly more than 100% yield crude, and the ratio of the intensities of the aromatic and cage proton resonances is 5.00:7.85.

D. Thermal Fragmentations of Alkylphosphoranes. All of the phosphoranes isolated above or generated as reaction intermediates, with the exception of **31,** fragment thermally to a tertiary phosphine and two olefins (eq 4–6, and Scheme VI). Table III summarizes the

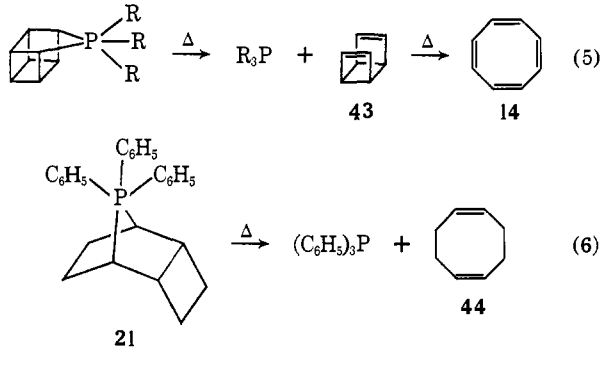


Table III. Thermal Fragmentation in C_6D_6 Solution

Phosphorane	Diene products[a,b]	Phosphine product[a]	Temp, °C	$t_{1/2}$, hr[c]
3	**43**[d] + **14**	$(C_6H_5)_3P$	75	7.0
3	**43** + **14**	$(C_6H_5)_3P$	60	50
4	**43** + **14**	$(C_6H_5)_2PCH_3$	75	23
5	**43** + **14**	$C_6H_5P(CH_3)_2$	75	36
6	**43** + **14**	$(CH_3)_3P$	75	108
21	**44**	$(C_6H_5)_3P$	75	0.6

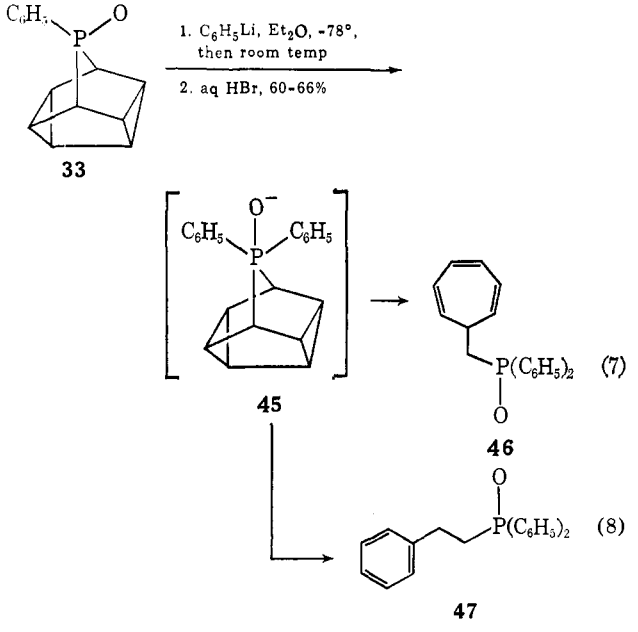
[a] Products were identified by proton nmr spectroscopy. [b] **43** on heating[29] rearranges to cyclooctatetraene (**14**) and the half-life at 75° is 7.5 hr (see Experimental Section). Thus **43** is detectable as a product only early in the reactions. [c] The rate of change of the ratio of a phosphorane resonance and the resonance of an internal standard was measured. [d] Reference 29.

thermal behavior in C_6D_6 solution of the phosphoranes that have been isolated. The phosphoranes **3** and **21** were also thermolyzed *in vacuo*. Thus **3** at 120° for 10 min gives in 85% yield a 4:1 mixture of *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**43**)[29] and **14** as the only volatile materials. The composition of the mixture was shown by the ratio of the sum of the intensities of the two nmr singlets of **43** at τ 4.03 and 7.00 and the singlet of **14** at τ 4.33 being 4.0. Similarly, **21** gives cycloocta-1,5-diene (**44**) in 94% yield after 5 min at 125°. Both **3** and **21** also yield triphenylphosphine.

No similar fragmentation of **31** to trimethylphosphine and cycloocta-1,5-diene was observed.

E. Photolysis of Phosphoranes 3 and 6. The ultraviolet spectra of **3** and **6** are displayed in Figure 3. Photolyzing the triphenylphosphorane **3** in C_6D_6 at room temperature using Pyrex-filtered light gives only *syn*-tricyclooctadiene, **43**, and no cyclooctatetraene, **14**. The conversion (nmr analysis) is 48% after 6 hr, and the diene was isolated pure in 15% yield after a similar photolysis of **3** in methylene chloride. Similarly photolyzing **6** in C_6D_6 through Pyrex gives **43** (37% after 51 hr) and trimethylphosphine (nmr analysis). A polymer begins to appear after 7 hr. Photolysis of **6** in cyclohexane also gives **43**.

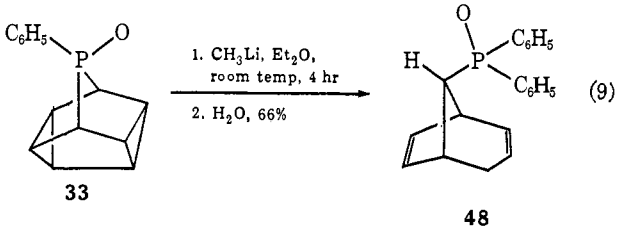
F. Skeletal Rearrangements. Phosphine oxide **33** with phenyllithium does not give as a stable product oxyphosphorane **45,** and hence after quenching with aqueous HBr the corresponding diphenylphosphonium salt, but gives instead in 66% yield (eq 7) **46,** a skeletal rearrangement product of **45.** A different rearrangement product, **47,** an isomer of **46,** is formed in 60% yield if in place of commercial phenyllithium solution in benzene–ether (70:30), specially purified phenyllithium in ether[30] is used (eq 8). Methyllithium with



33 also gives (in 66% yield) a skeletal rearrangement product **48** (eq 9).

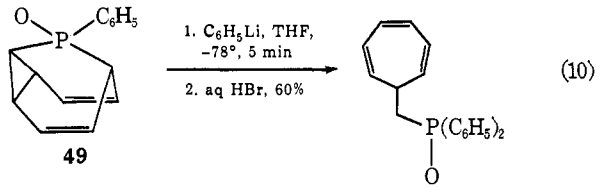
The reaction of phenyllithium with another bridged

(29) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).
(30) M. Schlosser and V. Ladenberger, *J. Organometal. Chem.*, **8**, 193 (1967).



33 48 (9)

phosphine oxide (**49**)[13] also gives a rearrangement product in 60% yield, and this is in fact compound **46** above (eq 10).



49 46 (10)

The structure of **46**, suggested by its spectroscopic properties, was verified by its synthesis from tropylium fluoroborate and the ylide of methyldiphenylphosphine oxide.[31] Structure **47** is a known material.[32] Structure **48** was identified by comparing its proton nmr spectrum with that of the parent hydrocarbon **50**[33] (Table IV).

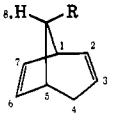
Discussion

The explanation advanced[7,10] to account for why alkylphosphoranes like **1**, **3**, **4**, **5**, **6**, and **21** are stable, while pentamethylphosphorane is not, is that a carbon–phosphorus–carbon angle in each precursory phosphonium salt is constrained by the ring system to much less than the tetrahedral angle[34] and that this strain is relieved when the pentavalent phosphorane forms. Moreover, once the strain is relieved in this way, the pentavalent phosphorane does not revert to a cyclic phosphonium salt since the strain would be restored. The usual reaction of an alkylphosphonium salt with an organolithium reagent, giving an ylide, apparently does not relieve the strain, ylides having approximately tetrahedral geometry.[37]

An alternative explanation, that the bridged ring system instead of promoting formation of the pentavalent phosphorane inhibits formation of the ylide, presumably by inhibiting the ylide's unshared carbon orbital from overlapping with an appropriate unfilled orbital on phosphorus, might account for the formation of **3** and **21**. However, this explanation does not account for the stability of alkylphosphoranes like **6**, as it is inconsistent with the observation that in 0.27 *N* NaOD the methyl protons in phosphonium salt **8** exchange with deuterons 44 times faster than those in tetramethylphosphonium iodide, implying that in the homocubane ring system as compared to the parent tetramethylphosphonium ion formation of an ylide is not only uninhibited, but promoted. This explanation also does not tally with the stability of known bridgehead sulfur ylides,[8] one example forming 10^3 as fast as an acyclic model compound.[8b] Moreover, it doesn't explain the reaction shown in Scheme II of phosphine oxide **9** with phenyllithium and HBr giving diphenylphosphonium salt **2**, while an explanation based on the relief of angle strain does.

While methyldiphenylphosphine oxide with organolithium reagents gives the ylide of methyldiphenylphosphine oxide,[31] and not a phosphonium salt, the formation of **2** from **9** might be accounted for if bridgehead hydrogens are nonacidic, **2** forming by default. However, triphenylphosphine oxide, which also cannot yield an ylide, with phenyllithium and HBr does not give tetraphenylphosphonium bromide,[38] suggesting that the reaction giving **2** is effective not because a side reaction, the formation of an ylide, has been suppressed, but because the relief of angle strain, which occurs when the organolithium reagent attacks phosphorus, drives the reaction of **9** to **51**. While the reaction of a phosphine oxide with an organolithium to give a phosphonium salt is uncommon, the reverse,

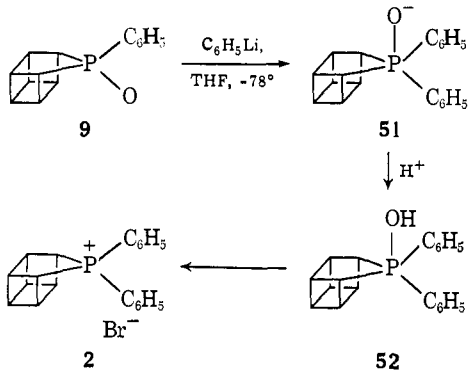
Table IV. Proton Nmr Spectra of **48** and **50**



Proton	**48**[a] (R = $PO(CH_3)C_6H_5$)	**50**[b] (R = H_{6b})
A. Chemical Shifts (τ)		
1	6.98	7.43
2	4.28	4.08
3	4.64	4.85
4 exo	7.22	7.83
4 endo	8.19	8.21
5	7.34	7.43
6	4.10	4.35
7	3.70	3.82
8	7.52	8.10, 8.34
P-CH_3	8.23	
P-aromatic (ortho)	2.29	
P-aromatic (meta and para)	2.50	
B. Observable Coupling Constants[c]		
$J_{1,6a}$	4.0	4.6
$J_{1,6b}$		<2.0
$J_{2,3}$	10.0	10.0
$J_{4exo,4endo}$	18.5	18.3
$J_{6,6}$	3.0	2.6
$J_{1,7}$	2.8	2.8
$J_{6,7}$	5.6	5.6
J_{P,CH_3}	12.5	
$J_{P,8a}$	4.0	
$J_{P,6}$	2.0	
$J_{P,ortho}$	11.0	

[a] At 100 MHz, ^{31}P decoupled. [b] At 220 MHz, from ref 33. [c] Absolute values, in Hz.

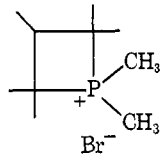
(31) J. J. Richard and C. V. Banks, *J. Org. Chem.*, **28**, 123 (1963).
(32) A. M. Aguiar and D. Daigle, *ibid.*, **30**, 2826 (1965).
(33) T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **93**, 1049 (1971); J. M. Brown and J. L. Occolowitz, *J. Chem. Soc. B*, 411 (1964); J. M. Brown and E. N. Cain, *J. Amer. Chem. Soc.*, **92**, 3821 (1970); S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *ibid.*, **89**, 3656 (1967); W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).
(34) The bridge angle in homocubyl *p*-bromobenzoate is 98°,[35] and since carbon–phosphorus bonds are about 1.85 Å long, while carbon–carbon bonds are 1.56 Å long, the bridge angle in **2** should be much less than 98°. In one bicyclo[2.2.1]heptene in which the one-atom bridge is a tetracoordinate phosphorus, the angle is 87°.[36]
(35) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *J. Amer. Chem. Soc.*, **93**, 1446 (1971).
(36) Y. H. Chiu and W. N. Lipscomb, *ibid.*, **91**, 4150 (1969).
(37) J. C. G. Bart, *J. Chem. Soc. B*, 350 (1969).
(38) (a) G. Wittig and H. J. Cristau, *Bull. Soc. Chim. Fr.*, 1293 (1969); (b) H. Gilman and G. E. Brown, *J. Amer. Chem. Soc.*, **67**, 824 (1945).



9 51 2 52

exemplified by **2** giving **52**, **51**, and then **9**, is a common reaction of phosphonium salts with aqueous base.[39]

That the acidity of the methyl protons in methylphosphonium salts is not inhibited when other bonds to phosphorus are constrained in a small ring, indicated by the methyl protons of **8** exchanging with deuterons more rapidly than the methyl protons in tetramethylphosphonium iodide,[28] has precedent in the methyl groups of **53** also exchanging more rapidly than those



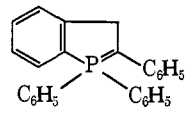
53

of tetramethylphosphonium iodide.[40] The phenyl group in **7** also should not inhibit the acidity of the methyl protons, as replacing the methyls of tetramethylphosphonium ion with phenyls increases the rate of exchange about 20-fold per phenyl group.[41]

The bridgehead protons in **8** exchange with 1 *N* LiOD more slowly than the methyl protons, possibly reflecting the decreased resonance stabilization afforded the anion under the constraints of the bridged ring system, or possibly reflecting the decrease in rate in acyclic systems with which protons on tertiary as compared to primary carbons exchange.[42] In the salt **2** the increased acidity expected when methyl substituents are replaced by phenyls[41] should counteract these effects, but the rate at which the bridgehead hydrogens in **2** exchange could not be measured directly as **2** hydrolyzes too rapidly to the phosphine oxide **9**. The exchange of the bridgehead hydrogens in the dimethyl salt, unlike the diphenyl salt, could be observed in 1 *N* LiOD at 100° as the former does not hydrolyze.

Whether a cyclic phosphonium salt reacts with an organolithium reagent to give an ylide or a pentasubstituted phosphorane should depend on the ring angle at the phosphorus, and if so, the angle below which pentasubstituted phosphoranes form and above which ylides form is bracketted between that in the bicyclo[4.2.1]nonane and the bicyclo[2.2.1]heptane ring systems. Thus **24a** with phenyllithium gives the ylide, **25**, while **20**, which differs from **24a** by only one bond, gives phosphorane **21** instead. Congruent with these results is the failure to prepare the diphenylphosphonium salt **24a** from phosphine oxide **22**, phenyllithium, and HBr and the success of the analogous preparation of salt **20** from phosphine oxide **19**.

The first reported example of a cyclic phosphorus ylide is **54**, and that it forms from the corresponding



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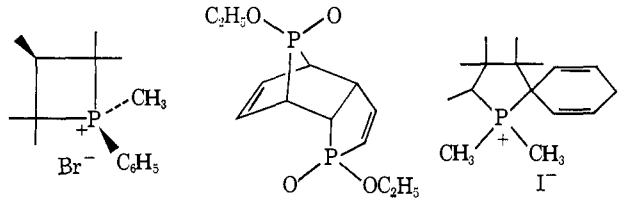
phosphonium salt and phenyllithium[43] is consistent with **24a** and phenyllithium giving an ylide. That diphenylphospholanium bromide (**42a**) with phenyllithium gives the ylide, reported above, is also consistent. The internal angle of a four-membered ring should be similar to the bridge angle in a bicyclo[2.2.1]heptane, and in fact X-ray analyses show the angle at phosphorus to be 83° in **55**[44] and 87° at the



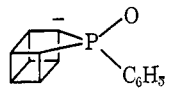
55 56 57

bridge in **56**.[36] These angles are much smaller than unbridged five-membered rings, 96° in **56**[36] and 100° in **57**.[45] A four-membered ring phosphonium salt might therefore be expected to react with organolithiums to give a pentavalent phosphorane. However, while in agreement with this **55** with phenyllithium[46] or *n*-butyllithium[47] does not give the corresponding ylide, pentasubstituted phosphoranes seem to be transient intermediates and not stable products.[46,47]

Methoxyphosphoranes with small rings, such as **13**, should also be more stable than acyclic analogs, but tetraalkylalkoxyphosphoranes are very unstable with respect to tetraalkylphosphonium alkoxides,[48] and the ring system does not seem to stabilize **13** sufficiently to make it easily isolable. Thus the reaction of **12** with methyllithium, which initially should give **13**, ultimately gives **6**, the reaction product of dimethylphosphonium salt **8** with methyllithium.

That the phosphine oxides **9** with phenyllithium and **10** with methyllithium at −78° give phosphonium salts **2** and **8** rather than ylides is uncommon, but the sensitivity of the reaction is remarkable. At room temperature rather than −78°, phosphonium salts are not formed: instead ylides are, **9** giving **58** and **10** giving **59**. Oxide **9** with methyllithium (rather than phenyllithium) also gives **59**. Direct conversions of

(39) (a) W. E. McEwen, G. Axelrad, M. Zanger, and C. A. Vander Werf, *J. Amer. Chem. Soc.*, **87**, 3948 (1965); (b) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).
(40) S. E. Cremer and C. H. Chang, *Chem. Commun.*, 1456 (1969).
(41) S. E. Cremer and R. J. Chorvat, *Tetrahedron Lett.*, 419 (1966).
(42) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 20 ff.
(43) G. Märkl, *Z. Naturforsch. B*, **18**, 84 (1963).
(44) C. Moret and L. M. Trefonas, *J. Amer. Chem. Soc.*, **91**, 2255 (1969).
(45) J. N. Brown and L. M. Trefonas, *J. Heterocycl. Chem.*, **9**, 463 (1972).
(46) S. E. Cremer and R. J. Chorvat, *Tetrahedron Lett.*, 413 (1968).
(47) J. R. Corfield, M. J. P. Harger, J. R. Shutt, and S. Trippett, *J. Chem. Soc. C*, 1855 (1970).
(48) An ingenious synthesis of $(CH_3)_4POCH_3$ has recently been reported: H. Schmidbaur and H. Stühler, *Angew. Chem., Int. Ed. Engl.*, **11**, 145 (1972).



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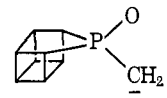

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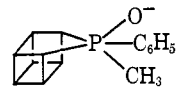
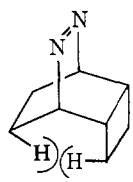
arylphosphine oxides to alkylphosphine oxides with alkyllithiums are rare,[49] having been limited to phosphine oxides that have no acidic hydrogen attached to the carbon adjacent to phosphorus.[46,50] Presumably all these reactions initially yield pentavalent oxyphosphoranes, such as **60**, but organolithiums must elimi-



60

nate from these easily. Oxyphosphoranes should eliminate organolithiums more easily than do pentaalkylphosphoranes because the resulting tetracoordinate phosphorus species enjoy a strong phosphorus–oxygen bond. That **60** eliminates phenyl rather than methyl or the ring residue and that **51** similarly eliminates phenyl rather than a ring residue is in accord with analogous results that occur when phosphonium salts hydrolyze in aqueous base.[39b]

That phenylphosphine oxide **19** (Scheme V) with methyllithium gives the corresponding methylphosphine oxides, **26A** and **26B**, can be accounted for similarly. However, these methylphosphine oxides with methyllithium give neither of the products analogous to those formed from **10**, a dimethylphosphonium salt or an ylide, but give the ring-cleaved product **27** instead. Possibly the conversion of **19** to **26A** and **26B** reflects the superior leaving ability of phenyl compared to the ring residue, while the converson of **26A** and **26B** to **27** reflects the superior leaving ability of the ring residue compared to methyl. The superior leaving ability of this ring residue compared to the ring residue that would have to be eliminated if **10** with methyllithium gave a product analogous to **27** might then be accounted for in the same way as the increased facility with which **61** compared to **62** eliminates nitrogen.[51]



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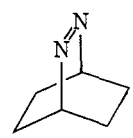

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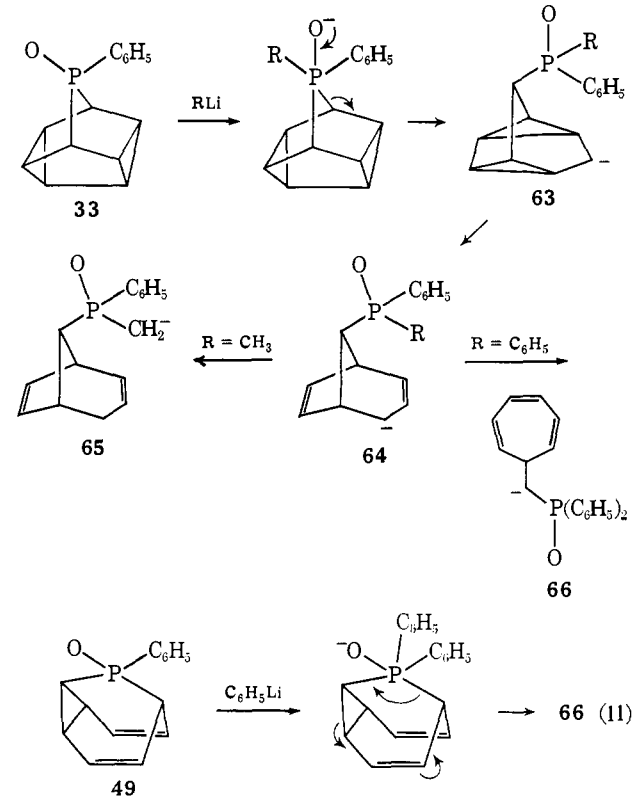
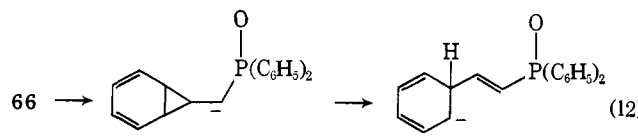
The latter effect has been attributed to the relief of steric interactions indicated on structure **61**.[51] That **30** with methyllithium gives **28** might be accounted for similarly, **31** being an intermediate whose ring cleaves particularly easily.

Scheme VII may account for phenylphosphine oxide **33** with phenyllithium giving **46** and with methyllithium **48**. From what is known about the parent

Scheme VII



hydrocarbon, **63** and **64** should interconvert quickly,[52] and they may even be resonance forms. The reason the paths followed differ when the reagents are methyllithium and phenyllithium may be either because $(C_6H_5)_2P(O)\bar{C}H-$ is a better leaving group than $(C_6H_5)(CH_3)P(O)\bar{C}H-$,[53] or because although an ylide **65** can be formed easily without further ring cleavage when R = CH_3, an analogous ylide cannot form when R = C_6H_5. Instead the ring cleaves giving ylide **66**. The reason that the skeleton of **33** with organolithiums rearranges at all, while under similar conditions **9** does not, is either because the reaction giving **63** is especially facile, or because the reactions of **33** proceeding to ylides are easy and irreversible. The reaction of **49** with phenyllithium can be accounted for similarly (eq 11). Whether the rearrangement is concerted is not known. We have not studied why the reactions giving **46** and **47** differ, but **66** is a plausible precursor of both products. A path from **66** to **47** is indicated in eq 12.



The thermal and photochemical fragmentations of alkylphosphoranes to two olefins and a tertiary phosphine may be cheleotropic reactions,[54] but we have no

(49) The conversions have frequently been effected by reducing the phosphorus–oxygen bond of arylphosphine oxides, quaternizing with alkyl halide, and hydrolyzing with aqueous alkali.[22]

(50) (a) D. Seyferth, D. E. Welch, and J. K. Heeren, *J. Amer. Chem. Soc.*, **86**, 1100 (1964); (b) W. Hawes and S. Trippett, *J. Chem. Soc. C*, 1465 (1969).

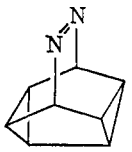
(51) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 387 (1972).

(52) S. Winstein, "Aromaticity: An International Symposium Held at Sheffield on July 6–8, 1966," The Chemical Society, London, 1967, p 5 ff.

(53) Methylphosphonium salts increase in acidity as the remaining substituents on phosphorus are changed from methyl to phenyl.[41] It is also conceivable that steric interactions are greater in **64** when R = C_6H_5 and are relieved when **66** forms.

(54) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

evidence for their concertedness. These reactions would have been especially interesting if they had yielded cubane, but they do not. The quickening of the thermal fragmentation reaction (eq 5) as methyl substituents are replaced by phenyls should be expected whether or not the reaction is concerted, if phenyls conjugatively delocalize electrons freed from two center bonds. That phosphoranes **37** and **41** are not sufficiently stable to be isolated, while **3–6** and **21** are, is in accord with the instability of **67** and **68** compared



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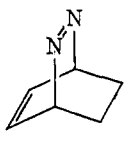

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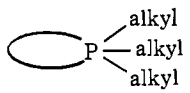
to **61** and **62**.[55] That **40**, unlike the bicyclo[4.2.1]-nonane **24a**, with phenyllithium (eq 4) does not yield an ylide quantitatively, but gives products derived from a phosphorane, may be accounted for if the formation of ylides is preceded by the reversible formation of phosphoranes and if **41** fragments to **14** and **38a** rapidly.

An interesting feature of the nmr spectrum of **6** (shown in Figure 2c) is that although the methyls appear equivalent, no structure in which they are equivalent can be drawn. Similarly, the nmr spectra of **3** (Figures 1a and 1b) show the bridgehead protons to be equivalent even though they cannot be equivalent in any one structure. This implies that the structure of these molecules rapidly reorganize intramolecularly so as to have a plane of symmetry on a time average. The barrier to this process was estimated by proton nmr spectroscopy at temperatures as low as $-184°$ to be about 5 kcal/mol in **5** and **6**.[56] The barrier could not be measured for **3** because it is insufficiently soluble at low temperatures.

Summary

The first pentaalkylphosphorane, **6**, has been synthesized by combining **8** with methyllithium. This reaction succeeds despite the acidity of the methyl protons because it relieves angle strain. This suggests that alkylphosphoranes in general should be preparable if two of the substituents are constrained in a ring that is sufficiently small, as in **69**. The bicyclo[2.2.1]-



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heptane ring system is small enough, but the bicyclo-[4.2.1]nonane ring system is too large. **25** is the first bridgehead phosphorus ylide to be prepared.

The reason that pentavalent alkylphosphoranes or bridgehead phosphorus ylides have not been synthesized previously is possibly because bridged phosphorus compounds are rare.[57] The synthesis summarized in Scheme III makes a number of such compounds easily available.

Experimental Section

General. Reactions of phosphonium salts with organolithium reagents were conducted under N_2 in a flame-dried 50-ml, three-necked, round-bottomed flask equipped with a nitrogen inlet, serum cap, stopper, and magnetic stirrer. Commercial anhydrous diethyl ether was used without further drying. Tetrahydrofuran (THF) was dried over potassium hydroxide pellets and distilled from $LiAlH_4$ onto Linde Type 5A molecular sieves. Benzene was dried by refluxing over sodium and was distilled onto Type 4A molecular sieves. Commercial methyl iodide was distilled and stored over a strip of copper. Hexachlorodisilane (Si_2Cl_6) from Matheson Coleman and Bell was used without purification. Phenyllithium was obtained as a 2.2–2.3 *M* solution in 70:30 benzene–ether from Alfa Inorganics, Beverly, Mass. Methyllithium was obtained as a 1.6 *M* solution in diethyl ether containing 0.4% LiCl from Foote Mineral Co., Exton, Pa. Dry solvents and reagents sensitive to air or moisture were transferred by syringe.

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or by Galbraith Laboratories, Inc. Knoxville, Tenn. Unless otherwise stated, spectroscopic data were determined using the following instruments: nmr, Varian A-60A (TMS, in τ units) or HA-100; ir, Perkin-Elmer 621; uv, Cary 14; mass spectra, Perkin-Elmer Hitachi RMU-6D or Jeol JMS-07 and are at 75 eV.

Cyclooctatetraene is abbreviated as COT.

Homocubyltriphenylphosphorane (3). Diphenylphosphoniahomocubane bromide (**2**) (1.00 g, 2.72 mmol) was suspended in 10 ml of dry THF and stirred rapidly with 1.25 ml of 2.2 *M* (2.72 mmol) phenyllithium. After 1 hr water (*ca.* 15 ml) and ether (10 ml) were added. The aqueous layer was extracted twice with 10 ml of ether, and the combined ether layers were dried ($MgSO_4$) and stripped, leaving an oil that either crystallized spontaneously or on trituration with methanol. Recrystallization from cyclohexane gave 600 mg (60.5%), mp 113–116°. The reaction can be conducted more conveniently in ether. A similar run with 738 mg of **2** (2.0 mmol) in 20 ml of dry ether gave, after work-up as above and two recrystallizations from acetone, 472 mg (64.5%) of white crystals: mp 115–116.5°; δ ^{31}P (C_6D_6, 85% external H_3PO_4, Bruker HX 90) = +53 ppm; ir (KBr) 3060 (m), 3000 (m), 2980 (s), 2963 (s), 1484 (m), 1434 (s), 1428 (s), 1421 (m), 1105 (s), 1060 (s), 990 (m), 924 (m), 745 (m), 700 (s), 555 (s), 510 (s); mass spectrum (parent peak and all peaks $\geq$10% intensity) *m/e* (rel intensity) 366 (M^+, 6), 289 (19), 263 (46), 262 (60), 261 (30), 185 (26), 184 (31), 183 (37), 152 (21), 115 (16), 109 (44) 108 (100), 107 (46), 104 (14), 103 (44), 78 (15), 77 (38), 52 (19), 51 (46), 50 (21).

An analytical sample was prepared by recrystallizing twice from cyclohexane and drying at room temperature (0.1 mm), mp 118–119°.

Anal. Calcd for $C_{26}H_{23}P$: C, 85.22; H, 6.33; P, 8.45. Found: C, 85.13; H, 6.43; P, 8.40.

Homocubyldiphenylmethylphosphorane (4) from Diphenylphosphoniahomocubane Bromide (2). Diphenylphosphoniahomocubane bromide (**2**) (369 mg, 1.0 mmol) was suspended in 5 ml of anhydrous ether and stirred rapidly with 0.63 ml (1.0 mmol) of methyllithium. After 3 hr at room temperature 5 ml of water was added. The aqueous layer was extracted (3 × 10 ml) with ether, and the combined ether layers were dried ($MgSO_4$) and stripped at room temperature, leaving 226 mg (75%) of white solid: mp range 103–120°; mass spectrum (parent peak and peaks $\geq$10% intensity) *m/e* (rel intensity) 304 (M^+, 1.0), 200 (25), 185 (12), 183 (20), 181 (47), 165 (12), 153 (17), 152 (30), 151 (10), 149 (10), 121 (10),

(55) **67** and **68** are also too unstable to isolate: L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5765 (1970); R. Askani, *Tetrahedron Lett.*, 3349 (1970); and N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *J. Amer. Chem. Soc.*, **91**, 5668 (1969). However, diazabasketene, like the homocubylphosphoranes, is isolable and stable: J. P. Snyder, *Diss. Abstr.*, **26**, 5728 (1966); R. Askani, *Chem. Ber.*, **102**, 3304 (1969).

(56) C. H. Bushweller, H. S. Bilofsky, E. W. Turnblom, and T. J. Katz, *Tetrahedron Lett.*, 2401 (1972).

(57) (a) E. H. Braye, W. Hübel, and I. Caplier, *J. Amer. Chem. Soc.*, **83**, 4406 (1961); (b) R. C. Cookson, G. W. A. Fowles, and D. K. Jenkins, *J. Chem. Soc.*, 6406 (1965); (c) M. Green, *ibid.*, 541 (1965); (d) R. Kluger, F. Kerst, D. G. Lee, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **89**, 3919 (1967); (e) G. Märkl and R. Potthast, *Tetrahedron Lett.*, 1755 (1968); (f) A. N. Hughes and S. Uaboonkul, *Tetrahedron*, **24**, 3437 (1968); (g) U. Schmidt, I. Boie, C. Osterroht, R. Schroer, and H. F. Grutzmacher, *Chem. Ber.*, **101**, 1381 (1968). (h) R. F. Mason and J. L. Van Winkel, French Patent 1502250 (1967); *Chem. Abstr.*, 70, 20221 (1969); (i) F. Mathey, R. Mankowski-Favelier, and R. Maillet, *Bull. Soc. Chim. Fr.*, 4433 (1970); (j) Y. Kashman and O. Awerbouch, *Tetrahedron*, **26**, 4213 (1970); (k) J. K. Stille, J. L. Eichelberger, J. Higgins, and M. E. Freeburger, *J. Amer. Chem. Soc.*, **94**, 4761 (1972).

115 (10), 107 (15), 104 (10), 103 (12), 91 (20), 81 (10), 79 (18), 78 (100), 77 (50), 76 (15), 75 (10), 74 (15), 65 (12), 63 (27), 59 (13), 57 (12), 55 (14), 52 (35), 51 (75), 50 (60), 49 (12).

An analytical sample was prepared by recrystallizing five times from anhydrous ether between room temperature and −78° and drying overnight over P_2O_5 at room temperature (0.1 mm), mp 124–125°.

Anal. Calcd for $C_{21}H_{21}P$: C, 82.87; H, 6.96; P, 10.18. Found: C, 82.62; H, 6.88; P, 10.30.

Homocubyldiphenylmethylphosphorane (4) from Methylphenylphosphoniahomocubane Iodide (7). Methylphenylphosphoniahomocubane iodide (**7**) (354 mg, 1.0 mmol) was suspended in 5 ml of anhydrous ether and stirred rapidly with 0.44 ml (1.0 mmol) of phenyllithium solution. After 3 hr at room temperature water (5 ml) was added. The aqueous layer was extracted (3 × 10 ml) with ether, and the combined ether layers were dried ($MgSO_4$) and stripped at room temperature, leaving 150 mg (50%) of white solid, mp range 107–123°. The nmr spectrum of the crude material was the same as that of the crude material prepared by the alternate route above except for some differences in the nmr intensities. Normalized to 21, the intensities were aromatics:cage:methyl 11.15:7.65:2.20.

Homocubyldimethylphenylphosphorane (5). Dimethylphosphoniahomocubane iodide (**8**) (292 mg, 1.0 mmol) was suspended in 5 ml of anhydrous ether and stirred rapidly with 0.44 ml (1.0 mmol) of phenyllithium solution. After 1 hr at room temperature water (5 ml) was added. The aqueous layer was extracted (3 × 10 ml) with ether, and the combined ether layers were dried ($MgSO_4$) and stripped at room temperature, giving after distillation [60° (10^{-6} mm), bulb to bulb] 133 mg (55%) of a slightly yellow oil. The compound discolors on exposure to air. Mass spectrum (parent peaks and peaks ≥10% intensity) *m/e* (rel intensity) 242 (3), 241 (8), 165 (18), 139 (13), 138 (100), 123 (55), 121 (20), 104 (19), 103 (21), 91 (24), 79 (14), 78 (82), 77 (33), 52 (53), 51 (20), 50 (47).

Homocubyltrimethylphosphorane (6). Dimethylphosphoniahomocubane iodide (**8**) (292 mg, 1.0 mmol) was suspended in 5 ml of anhydrous ether and stirred rapidly with 0.63 ml (1.0 mmol) of methyllithium in ether. The suspension was stirred for 3 hr at room temperature and quenched with 5 ml of water. The aqueous layer was extracted (3 × 5 ml) with ether. The ether layers were dried ($MgSO_4$) and stripped at room temperature, leaving an oil that was immediately distilled at room temperature (10^{-6} mm) into a trap cooled with liquid N_2, giving 35 mg (20%) of product. The yields in several experiments ranged between 20 and 25%. The compound discolors after exposure to air for a few days. (Extracting the aqueous layer with chloroform (4 × 10 ml) gave *ca.* 30% of recovered salt (**8**).) ^{31}P nmr Bruker HX90 (C_6D_6, external 85% H_3PO_4) δ + 90 ppm; ^{13}C nmr (C_6D_6, TMS, Jeol JNM-PS-100) δ 22.07 (d, $|J_{PC}|$ = 49.0 Hz, P-CH_3), 38.31 (d, $|J_{PC}|$ = 5.28 Hz), 44.41 (d, $|J_{PC}|$ = 43.8 Hz), 48.41 (d, $|J_{PC}|$ = 14.1 Hz); ir (neat) 2955 (s), 2880 (w), 2810 (w), 1420 (w), 1270 (m), 1240 (m), 1057 (s), 952 (s), 915 (m), 832 (m), 662 (m), 525 (s), mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) 180 (M^+, 47), 153 (13), 152 (25), 104 (50), 103 (35), 102 (10), 79 (10), 78 (100), 77 (33), 76 (35), 75 (18), 74 (15), 63 (20), 62 (10), 61 (57), 59 (50), 58 (13), 57 (35), 56 (10), 52 (22), 51 (43), 50 (35), 46 (40), 45 (15), 41 (10), 39 (35), 38 (13).

Reaction of Methylphenylphosphoniahomocubane Iodide (7) with Methyllithium. Methylphenylphosphoniahomocubane iodide (**7**) (354 mg, 1.0 mmol) was suspended in 5 ml of anhydrous ether and stirred rapidly with 0.63 ml (1.0 mmol) of methyllithium. After 3 hr at room temperature water (5 ml) was added. The aqueous layer was extracted (3 × 10 ml) with ether. The combined ether layers were dried ($MgSO_4$) and stripped, leaving 148 mg of a residue that was partly crystalline and partly oily. Nmr analysis showed it to be a mixture of three compounds: homocubyldiphenylmethylphosphorane (**4**, 20%), homocubyldimethylphenylphosphorane (**5**, 63%), and homocubyltrimethylphosphorane (**6**, 17%). The three compounds were identified by comparing the chemical shifts and coupling constants of their methyl doublets with those of the authentic samples. The per cent composition was determined by averaging five integrations of the methyl resonances. In one run **4** was isolated as a solid, mp 120–123°, from the mixture after crystallization from ether at −78° and was identified by its nmr spectrum.

Diphenylphosphoniahomocubane Bromide (2). A 200-ml, three-necked, round-bottomed flask equipped with a nitrogen inlet, serum cap, stopper, and magnetic stirrer was flamed under a nitrogen stream. Phenylphosphahomocubane oxide (**9**) (3.30 g, 14.5 mmol) and 65 ml of dry THF were added. The solution was cooled to −78° (some material precipitated) and 6.6 ml of 2.2 *M* (14.5 mmol) phenyllithium was added. The resulting violet solution was allowed to stir for 5 min at −78° and was quenched with 6.5 ml of 20% aqueous HBr at −78°, the color discharging. The resulting white slurry was allowed to warm to room temperature. About 50 ml of ether was added to the slurry and the ether–THF layer decanted from the solid residue. The residue was washed twice with ether, dissolved in excess methanol, and stirred with solid sodium carbonate to remove traces of HBr. The solution was filtered and stripped, leaving slightly yellow crystals, which were recrystallized from methanol–ether giving 3.20 g (60%) of product, mp 310–311°. The yield in several experiments ranged from 55 to 73%: nmr (CF_3CO_2H) 2.23 (m, 10.07 H), 5.40 (m, 1.73 H), 5.97 (m, 6.20 H); ir (KBr) 3072 (w), 2991 (s), 1584 (m), 1490 (w), 1440, (s), 1350 (w), 1255 (s), 1245 (s), 1120 (s), 1110 (s), 999 (s), 860 (m), 765 (s), 740 (m), 706 (s), 691 (m), 550 (s), 526 (s).

Recrystallization from hot water followed by drying at 100° (0.05 mm) over P_2O_5 overnight gave an analytical sample, mp 310–311°.

Anal. Calcd for $C_{20}H_{16}BrP$: C, 65.05; H, 4.91; Br, 21.46; P, 8.39. Found: C, 65.27; H, 4.91; Br, 21.77; P, 8.33.

The salt could also be prepared by combining the phosphine **11** with phenylmagnesium bromide and oxygen and then HBr[56] in 41% yield. It could not be prepared from **11** and bromobenzene with $NiBr_2$[21] at 200°.

Methylphosphahomocubane Oxide (10). A 500-ml, three-necked, round-bottomed flask equipped with a N_2 inlet, pressure equalizing addition funnel, serum cap, and magnetic stirrer was flamed under a N_2 purge. Anhydrous ether (200 ml) was added followed by 14.5 ml (23.2 mmol) of methyllithium in ether through the serum cap. A solution of 4.56 g (20.0 mmol) of phenylphosphahomocubane oxide (**9**) in 100 ml of anhydrous ether and 100 ml of dry benzene was added in drops over a 0.5-hr period to the solution cooled to 0°. The resulting orange solution was stirred at room temperature for 1 hr and hydrolyzed with 100 ml of water, discharging the color. The organic layer was extracted once with 25 ml of water. The combined aqueous layers were saturated with NaCl and extracted (5 × 100 ml) with chloroform. The combined chloroform layers were dried ($MgSO_4$) and stripped leaving a crystalline residue, which after sublimation at 90° (0.1 mm) gave 2.18 g (66%) of product. The yield ranged from 65 to 75% in several experiments: nmr ($CDCl_3$) 6.10 (m, 1.98 H), 6.57 (m, 6.04 H), 8.54 (d, $|J_{PH}|$ = 12.0 Hz, 2.98 H); ir (1% in CCl_4) 1187.0 (P-O); mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) 166 (M^+, 25), 133 (19), 105 (10), 104 (100), 103 (50), 78 (87), 77 (25), 63 (15), 62 (10), 52 (20), 51 (30), 50 (19), 47 (28).

An analytical sample was prepared by recrystallizing twice from cyclohexane and subliming at 90° (0.1 mm), mp 98.5–100°.

Anal. Calcd for $C_9H_{11}OP$: C, 65.05; H, 6.67; P, 18.65. Found: C, 64.63; H, 6.68; P, 18.56.

When the reaction was repeated using 1.0 mmol of **9** and 1.15 mmol of CH_3Li, but quenched with D_2O, the proton nmr spectrum of **10** showed that one deuterium had been incorporated into the methyl group. The average intensity ratio measured in five integrations of the cage proton and methyl proton resonances was 8:1.97.

Phenylphosphahomocubane (11). A 100-ml, three-necked, round-bottomed flask equipped with a reflux condenser, nitrogen inlet, serum cap, stopper, and magnetic stirrer was flamed out with a nitrogen purge. Phenylphosphahomocubane oxide (**9**) (2.30 g, 10.04 mmol) and 50 ml of dry benzene were added. Si_2Cl_6 (2.23 ml, 3.55 g, 13.2 mmol) was added to the stirred solution, which was then refluxed for 15 min, and cooled to 0°. The stopper was replaced by a pressure-equalizing addition funnel, and 30 ml of 30% aqueous NaOH solution was added (very slowly at first) while stirring rapidly. The layers were separated and the aqueous layer was extracted (3 × 25 ml) with benzene. Drying ($MgSO_4$) and stripping left an oil that slowly crystallized. Sublimation at 50° (0.1 mm) gave 1.15 g (55%) of product, mp 54.5–56.5°, identical (nmr) with that obtained previously by reducing **9** with $HSiCl_3$–Et_3N.[13]

Methylphenylphosphoniahomocubane Iodide (7). Phenylphosphahomocubane (**11**) (808 mg, 3.81 mmol) was dissolved in 20 ml of benzene in a 50-ml, round-bottomed flask equipped with a magnetic stirrer and N_2 inlet. Methyl iodide (1.77 ml, 2.70 g, 19.1 mmol, 5 × excess) was added in one portion to the stirred solution. A precipitate formed instantly. After stirring for 5 hr at room

(58) J. Dodonow and H. Medox, *Chem. Ber.*, **61**, 907 (1928).

temperature, filtering, washing with benzene, and air drying gave 1.28 g (95%) of crude product, which was recrystallized from 95% ethanol and dried overnight over P_2O_5 at 100° (0.1 mm): nmr ($CDCl_3$–CD_3OD) 2.26 (m, 4.95 H), 5.16 (m, 1.87 H), 5.90 (m, 1.87 H), 6.25 (m, 4.28 H), 7.63 (d, $|J_{PH}|$ = 14.0 Hz, 3.08 H).

An analytical sample was prepared by recrystallizing four times from 95% ethanol and drying overnight over P_2O_5 at 100° (0.1 mm), mp 195–196°.

Anal. Calcd for $C_{15}H_{16}IP$: C, 50.87; H, 4.55; I, 35.83; P, 8.75. Found: C, 50.82; H, 4.69; I, 35.52; P, 8.68.

Dimethylphosphoniahomocubane Iodide (8). A 200-ml, three-necked, round-bottomed flask equipped with a reflux condenser, N_2 inlet, serum cap, stopper, and magnetic stirrer was flamed with a N_2 purge. Methylphosphahomocubane oxide (**10**) (2.18 g, 13.2 mmol) in 60 ml of dry benzene was added, followed by 2.9 ml (4.60 g, 17.1 mmol) of Si_2Cl_6[14] through the serum cap. The solution was refluxed for 15 min and then cooled to 0°. The stopper was replaced by a pressure-equalizing addition funnel, and 50 ml of 30% sodium hydroxide solution was added in drops to the rapidly stirred solution. The layers were then separated, and the aqueous layer was extracted (3 × 40 ml) with benzene. The benzene layers were dried ($MgSO_4$) and concentrated to *ca.* 50 ml. Methyl iodide (3.3 ml, 7.52 g, 53 mmol, fourfold excess) was added while the benzene solution of the phosphine was stirred rapidly. The salt began to precipitate immediately. The mixture was stirred under N_2 for 3 hr. Filtration and air drying gave 3.08 g (80%) of product, which was recrystallized from 95% ethanol and dried at 100° (0.1 mm) over P_2O_5 overnight before further use: nmr ($CDCl_3$) 5.50 (m, 2.09 H), 6.02 (m, 4.03 H), 6.35 (m, 1.90 H), 7.75 (d, $|J_{PH}|$ = 14.5 Hz, 5.98 H).

An analytical sample was prepared by recrystallizing twice further from 95% ethanol and drying overnight at 100° (0.1 mm) over P_2O_5, mp 308–309° dec. The sample begins to decompose around 250°.

Anal. Calcd for $C_{10}H_{14}IP$: C, 41.14; H, 4.83; I, 43.45; P, 10.61. Found: C, 41.18; H, 4.77; I, 43.43; P, 10.64.

Phenylphosphahomocubane Oxide (9) with Phenyllithium at Room Temperature. A 50-ml, three-necked, round-bottomed flask equipped with a serum cap, nitrogen inlet, stopper, and magnetic stirrer was flamed under nitrogen. Phenylphosphahomocubane oxide (**9**) (228 mg, 1.0 mmol) was placed in the flask, and 10 ml of dry THF was added by syringe. The solution was treated with 0.5 ml of 2.3 *M* phenyllithium solution (1.2 mmol) and stirred for 10 min. A reddish-brown color developed which discharged when 1.0 ml of 24% HBr was added. No salt appeared. The aqueous layer was extracted (2 × 5 ml) with chloroform and the combined organic layers were dried (Na_2CO_3, $MgSO_4$). Stripping left 307 mg of yellow solid, whose nmr spectrum showed it to be only starting material and phenyllithium residue. When a similar reaction mixture was quenched after 20 min with D_2O, worked up as above, and chromatographed on 2 × 21 cm silica gel using benzene and then 5% methanol in benzene as eluents, 172 mg of pale yellow solid was obtained. Recrystallization from 7:2 benzene–cyclohexane gave 108 mg of white crystals, which after sublimation at 115° (0.05 mm) gave 80 mg of pure material whose nmr spectrum is like that of the starting material, except that the intensity of the resonance at τ 6.5 is diminished. The intensities of the resonances at τ 2.5, 6.0, and 6.5 normalized to 12 were 5.00, 1.96, and 5.04. The 25-eV mass spectrum showed a base peak at *m/e* 105 (C_8H_7D) and peaks at *m/e* 228 (20% base) and 229 (8%). Undeuterated material has the base peak at *m/e* 104 and other peaks at 227 (31%) and 228 (8%).[19] Deuterium must have been incorporated into the caged ring. Assuming deuterium is incorporated adjacent to phosphorus the two-proton nmr resonance at τ 6.0 must be due to the γ and not the bridgehead hydrogens.

Methylphosphahomocubane Oxide (10) with Methyllithium at Room Temperature. A 50-ml, three-necked, round-bottomed flask equipped with a nitrogen inlet, serum cap, stopper, and magnetic stirrer was flamed under nitrogen. Methylphosphahomocubane oxide (**10**) (166 mg, 1.0 mmol) was placed in the flask and 10 ml of anhydrous ether added by syringe. The solution was treated with 1.2 ml (2.0 mmol) of methyllithium, whereupon gas evolved instantly. The solution became cloudy and slightly yellow, and after 15 min it was quenched with *ca.* 1.0 ml of 25% DBr in D_2O (enough to make the solution acidic to pH paper). About 1 ml of D_2O was then added and the aqueous layer was extracted (3 × 5 ml) with chloroform. Drying ($MgSO_4$) and stripping left 170 mg of a yellow oil, which solidified on standing. The nmr showed it to be only recovered phosphine oxide **10**, but the ratio of the intensities of the cage and methyl resonances was 8:1.55.

At −78°. Phosphine oxide **10** (100 mg, 0.6 mmol) in 5 ml of dry THF was treated with 0.5 ml (0.8 mmol) of methyllithium in the same apparatus at −78° for 5 min. The colorless solution was quenched with *ca.* 1 ml of 25% DBr in D_2O. Thawing to room temperature gave a clear one-phase solution. About 5 ml of ether was added, and the aqueous layer was extracted (3 × 5 ml) with chloroform. The combined organic layers were dried (Na_2CO_3, $MgSO_4$) and stripped, leaving (37 mg, 25%) yellow crystals of dimethylphosphoniahomocubane bromide (**8**) (containing no deuterium). The nmr spectrum of this bromide is similar to that of the iodide described above. The yield of the bromide may be low because the bromide may be more soluble than the iodide in water. No other products were detectable by nmr.

Homocubyltrimethylphosphorane (6) from Methoxy Salt 12. Methylphosphahomocubane oxide (**10**) (830 mg, 5.0 mmol) was dissolved in 20 ml of dry benzene in a 50-ml erlenmeyer flask containing a magnetic stirring bar. About 1.14 g (10.0 mmol) of methyl fluorosulfonate[17] was added, the flask stoppered, and stirring begun. A solid appeared in about 5 min. Stirring was continued for 1.5 hr, after which the benzene was decanted and pipetted away, leaving a somewhat oily solid, which was washed (2 × 5 ml) with benzene. Trituration with ether gave crystals, which were filtered, washed well with ether, and dried by suction, giving 1.22 g (87%) of methoxy salt **12**, mp 91–93°. The product appears to be hygroscopic and unstable, etching the glass container and smelling of SO_2 after *ca.* 1 day: nmr ($CDCl_3$) 5.98 (d, $|J_{PH}|$ = 11.5 Hz) superimposed on broad multiplet, 5.62–6.50 (11.15 H total), 7.86 (d, $|J_{PH}|$ = 13.5 Hz, 2.85 H).

A suspension of 140 mg of methoxy salt **12** (0.5 mmol) in 5 ml of ether was treated with 0.62 ml (1.0 mmol) of methyllithium for 1 hr and quenched with 5 ml of water. The aqueous layer was extracted (2 × 5 ml) with ether and (3 × 10 ml) with chloroform. Each layer was dried ($MgSO_4$) and stripped. The ether extract gave 40 mg (44.5%) of the trimethylphosphorane **6** (nmr) and the chloroform layer gave 40 mg (48%) of the methylphosphine oxide **10** (nmr). Yields are based on salt **12**. No other nmr signals, attributable to methoxyphosphorane **13**, could be detected.

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene (16). A 2-l., three-necked, round-bottomed flask equipped with a mechanical stirrer, distillation adapter with a N_2 inlet and outlet, and stopper was flamed under a N_2 purge. Lithium metal dispersion (13.7 g, 0.98 g-atom) (50% by weight in Amsco, particle size 200 μ, from Foote Mineral Co.) was added and the Amsco removed by five successive washings with dry pentane. After the last washing, the residual pentane was blown off with a N_2 stream. Anhydrous ether (1 l.) was added, and then 54 ml (50 g, 0.48 mol) of freshly distilled COT (bp *ca.* 42–44° at the aspirator) was added. The mixture was stirred overnight. (The color passes from yellow to green to brown, and the dianion ultimately precipitates as a white solid from a yellow-brown solution.)

A 3-l., three-necked, round-bottomed flask equipped with a mechanical stirrer, distillation adapter with N_2 inlet and outlet, and stopper was flamed under N_2 and mounted adjacent to the dianion flask. Anhydrous ether (500 ml) and 136 ml (179 g, 1.0 mol) of distilled dichlorophenylphosphine [Aldrich, bp 58° (0.3 mm); a forerun, bp 47–58° (0.3 mm), was discarded] were added and the solution was stirred and cooled to 0°. Tygon tubing was then connected to the nitrogen outlet of the 2-l. flask and the inlet of the 3-l. flask, and the outlet of the 3-l. flask was connected to an oil bubbler. The flasks were then connected by glass delivery tubes, the one in the 2-l. flask reaching to the bottom. By pinching the tygon tubing connecting the two flasks and controlling the N_2 flow, the dianion suspension was delivered to the phosphine solution. The addition was completed over a period of 10 or 15 min. Residual COT dianion was washed over with four 50-ml portions of ether, and the delivery tubes were removed and replaced with stoppers. (Caution: solid dianion caked on the tubes may ignite or spark in the air; the tubes should be plunged rapidly into a pail of water.) The N_2 lines and paraffin bubbler were removed and replaced by a direct N_2 inlet to the 3-l. flask. Residual dianion and lithium metal were destroyed with *tert*-butyl alcohol, then methanol, and finally water.

The yellow solution in the 3-l. flask was stirred for 0.5–1.0 hr at 0° and hydrolyzed (very slowly at first) with 250 ml of water added *via* an addition funnel. The mixture was neutralized with saturated sodium carbonate solution and suction filtered (Celite) to remove much insoluble material. The filter cake was leached well with ether. The aqueous layer of the filtrate was extracted twice with 250 ml of ether and the combined ether layers were dried ($MgSO_4$) and filtered into a 4-l. erlenmeyer flask. One quart of toluene

was added, and the solution with a N_2 stream bubbling vigorously through was placed on a steam bath. As the ether evaporated, and the temperature rose, the yellow solution became dark brown. Heating was continued for about 1 hr after the solution turned brown, and the remaining solvents were then removed on the rotary evaporator. The brown residue was distilled in an apparatus for distilling solids, bp 100–170° (0.2–0.4 mm), into a receiver packed in Dry Ice. The resulting pale yellow solid was recrystallized from methanol and dried at 0.2 mm. The yields in five experiments ranged between 55 and 70 g (54–69%), mp 84–86° (lit.[16] mp 85.5–86.5°). The nmr spectrum showed no impurity, except for traces of methanol, and was identical with that previously reported.[16] The compound was stored under nitrogen in the freezer.

9-Phenyl-9-phosphabicyclo[6.1.0]nonatriene (15). The procedure was identical with that used to prepare **16.** An experiment using a smaller but similar apparatus (500-ml flasks) and employing 1.40 g (0.102 g-atom) of lithium dispersion, 150 ml of ether, 5.40 ml (5.00 g, 0.048 mol) of COT, and 14 ml (18.4 g, 0.103 mol) of dichlorophenylphosphine was carried through to the point where the ether extracts were dried ($MgSO_4$) and filtered. The ether was then stripped at room temperature, leaving 8.46 g of yellow oil. Trituration with methanol afforded yellow crystals, which were filtered and washed several times with a litle methanol, giving 6.5 g (64%) of pale yellow crystals, mp 45–47° (recrystallization of the crude material from methanol between room temperature and −78° gives less pure material, mp 42–45°). The nmr is much cleaner than that previously reported:[16] τ 2.74 (m, 5.02 H), 3.96 (5 rather broad lines, 6.15 H), 7.40 (d, $|J| = 3.5$ Hz, 1.84 H). A sample stored for over 1 year under nitrogen in the freezer contained a little polymeric material that was insoluble in $CDCl_3$, but filtration gave a clear solution, whose nmr was unchanged. There was no sign of rearrangement product **16.**

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene Oxide (17). This oxide was prepared as originally described[16] by oxidizing **16** with 30% H_2O_2 in $CHCl_3$ at 0°. The following precautions were taken. After the oxidation mixture was diluted, the layers were separated; the aqueous layer was extracted twice with chloroform and the combined chloroform layer was washed once with aqueous $NaHSO_3$ to destroy any peroxides. The chloroform extract was then dried ($MgSO_4$), stripped, and the solid sublimed at 160° (0.05 mm) giving **17** in 90% yield, mp 181.5–183.5° (lit.[18] 182.8–183.4°). The nmr is identical with that previously reported;[16] ir (1% in $CHCl_3$–CCl_4) 1215.5 cm^{-1} (P–O).

Phenylphosphahomocubane Oxide (9). 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene oxide (**17**) (5.00 g, 21.9 mmol) was dissolved in 300 ml of ordinary benzene (by warming on a steam bath and then cooling to room temperature) and 100 ml of Spectrograde acetone was added. The solution was diluted to 1 l. with benzene and with nitrogen bubbling through was photolyzed through Corex for 40 hr with a 450-W medium-pressure Hanovia lamp. The solvents were concentrated to about 20–25 ml and applied to a 5 × 30 cm silica gel column and eluted with 5% methanol in benzene. A pale yellow band of COT moves rapidly through the column while the desired product moves more slowly as an orange-yellow band. Collection of this band and removal of the solvent left an orange-yellow solid, which was recrystallized twice from benzene–cyclohexane (7:2) giving 1.40–1.70 g (28–34%) of **9** pure enough for further transformations, mp 112–115° (sealed capillary). Sublimation at 105° (0.05–0.1 mm) gives slightly purer product, 23–27%, mp 115–118° (lit.[13] mp 122–123°). The nmr spectrum was identical with that previously reported;[13] ir (1% in CCl_4) 1190 cm^{-1} (P–O).

The mother liquors of several recrystallizations were concentrated, rechromatographed, and recrystallized, giving some additional material.

9-Phenyl-9-phosphatricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene Oxide (18). 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene oxide (**17**) (5.00 g, 21.9 mmol) was dissolved in 300 ml of ordinary benzene by warming on a steam bath and then cooling to room temperature, diluted to 1 l., and with N_2 bubbling through was irradiated through Pyrex for 2.75 hr with a 450-W medium-pressure Hanovia lamp. The benzene was stripped leaving a yellow crystalline residue, which was applied to a 5 × 30 cm silica gel column packed in benzene. Elution with 5% methanol in benzene and evaporation left a crystalline solid, which was recrystallized from benzene–cyclohexane (3:1) giving 2.50 g (50%) of pure **18**, mp 178–179° (lit.[13] mp 175–177°), identical (nmr) with that previously reported.[13]

9-Phenyl-9-phosphatricyclo[4.2.1.$0^{2,5}$]nonane Oxide (19). 9-Phenyl-9-phosphatricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene oxide (**18**) (2.50 g, 10.95 mmol) was dissolved in 55 ml of methanol and filtered to remove some insoluble particles. Platinum oxide (620 mg) was added, and the solution was hydrogenated at room temperature and atmospheric pressure. The catalyst was filtered and the methanol removed, leaving a brown solid. Sublimation at 135° (0.1 mm) gave white crystals, which were recrystallized once from benzene: yield 2.11 g (83%); mp 149–151°; nmr ($CDCl_3$) 2.50 (m, 4.75 H), 7.62 (m, 12.25 H); ir (1% in CCl_4), 1176.5 cm^{-1} (P–O); (KBr) 3051 (w), 2988 (m), 2951 (s), 2909 (m), 1590 (m), 1248 (m), 1219 (s), 1197 (m), 1170 (s), 1120 (s), 1065 (w), 1046 (w), 847 (w), 750 (s), 700 (s), 625 (w), 582 (s), 495 (s), 410 (s); mass spectrum (peaks >10% intensity) *m/e* (rel intensity) 233 ($M + 1$, 15), 232 (M^+, 100), 231 (26), 217 (15), 204 (24), 203 (10), 191 (11), 166 (10), 153 (10), 152 (10), 149 (18), 141 (14), 140 (15), 126 (13), 125 (39), 124 (13), 112 (11), 107 (20), 106 (17), 105 (15), 93 (13), 91 (37), 85 (14), 80 (44), 79 (93), 78 (30), 77 (65), 71 (10), 70 (13), 69 (10), 67 (30), 65 (15), 57 (21), 56 (11), 55 (20), 54 (27), 53 (15), 51 (32), 50 (10), 47 (30), 44 (15), 43 (15), 41 (35), 39 (32); uv_{max} (95% EtOH) 272 nm (ϵ 657), 265 (750), 258 (530), 253 (354), 218 (12,800).

An analytical sample was prepared by three further sublimations at 135° (0.1 mm), mp 152–154°.

Anal. Calcd for $C_{14}H_{17}OP$: C, 72.39; H, 7.38; P, 13.34. Found: C, 72.19; H, 7.27; P, 13.13.

9,9-Diphenylphosphoniatricyclo[4.2.1.$0^{2,5}$]nonane Bromide (20). A 50-ml, three-necked, round-bottomed flask equipped with a nitrogen inlet, stopper, serum cap, and magnetic stirrer was flamed under a nitrogen purge. 9-Phenyl-9-phosphatricyclo[4.2.1.$0^{2,5}$]-nonane oxide (**19**) (1.00 g, 4.32 mmol) was placed in the flask and dissolved in 30 ml of dry THF. After cooling to −78° (some precipitation occurring), 2.0 ml of 2.2 *M* (4.40 mmol) phenyllithium solution was added through the serum cap, and the pink-brown solution was stirred at −78° for 5 min and hydrolyzed with 2.0 ml of 25% HBr. The color discharged instantly affording a white suspension that was warmed to room temperature. The ethereal layer was decanted, and the solid was washed (3 × 20 ml) with ether. Recrystallization from methanol–ether gave 850 mg (53%): nmr ($CDCl_3$) 1.42 (m, ortho aromatics, 3.96 H), 2.37 (m, meta and para aromatics, 5.87 H), 5.32 (broad s, 1.96 H), 7.02 (m) and 7.75 (m) (10.18 H); ir (KBr) 3070 (w), 3005 (m), 2954 (s), 1620 (m), 1585 (w), 1440 (s), 1314 (m), 1244 (m), 1115 (s), 1105 (s), 1053 (m), 760 (s), 731 (s), 695 (s), 569 (s), 525 (s), 500 (m); uv_{max} (95% EtOH) 274 nm (ϵ 1490), 267 (1970), 261 (1550), 256 (shoulder 1120), 230 (20,400).

An analytical sample was prepared by recrystallizing five times from methanol–ether and drying overnight over P_2O_5 at 100° (0.1 mm), mp 264–265°.

Anal. Calcd for $C_{20}H_{22}BrP$: C, 64.35; H, 5.94; P, 8.30. Found: C, 64.10; H, 6.03; P, 8.31.

Phosphorane 21. 9,9-Diphenylphosphoniatricyclo[4.2.1.$0^{2,5}$]nonane bromide (**20**) (1.00 g, 2.68 mmol) was suspended in 25 ml of dry THF and stirred rapidly at room temperature as 1.22 ml of 2.2 *M* (2.68 mmol) phenyllithium solution was added through the serum cap. The suspension slowly gave way to a reddish-brown solution, which was stirred for 1 hr at room temperature and then hydrolyzed with 10 ml of water. The color discharged, leaving a clear organic layer. The layers were separated, and the aqueous layer was extracted (2 × 20 ml) with ether. Drying ($MgSO_4$) and stripping left a yellow oil, which was crystallized from acetone giving 432 mg. Concentration of the mother liquor gave an additional 215 mg or 647 mg (65%) total: nmr ($CDCl_3$) 2.85 (m, 15.15 H), and 7.45, 7.96, and 8.45 (overlapping multiplets, 11.85 H); ir (KBr) 3055 (w), 2935 (s), 1478 (s), 1436 (s), 1425 (s), 1322 (w), 1260 (w), 1085 (s), 1062 (s), 1022 (s), 1000 (m), 938 (w), 913 (w), 749 (s), 704 (s), 653 (s), 596 (s); mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) 370 (M^+, 1.5), 263 (20) 262 (100), 261 (15), 185 (10), 184 (15), 183 (67), 108 (33), 107 (13); uv_{max} (95% EtOH) 320 nm (plateau, ϵ 160), 275 (2120), 267 (2740), 262 (2380), 255 (sh, 1920), 228 (19,900).

An analytical sample was prepared by recrystallizing twice further from acetone and drying at room temperature (0.1 mm), mp 118–119°.

Anal. Calcd $C_{26}H_{27}P$: C, 84.29; H, 7.35; P, 8.36. Found: C, 84.42; H, 7.47; P, 8.53.

9-Phenyl-9-phosphabicyclo[4.2.1]nonane Oxide (22). 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene oxide (**17**) (2.00 g, 8.77 mmol) in 50 ml of methanol plus 175 mg of platinum oxide was hydrogenated at atmospheric pressure–room temperature. After 3 mol of hydrogen had been taken up, the catalyst was filtered, the methanol stripped, and the crystalline residue sublimed at 150° (0.1 mm) giving 1.75 g (85.5%): nmr ($CDCl_3$) 2.48 (m, 4.97 H), 7.22 (m, 4.32 H), 8.10 and 8.75 (m, 9.72 H); ir (1% in CCl_4) 1177.5

cm^{-1} (P–O); ir (KBr) 3050 (m), 2925 (s), 2916 (s), 2865 (m), 1590 (w), 1469 (s), 1447 (s), 1432 (s), 1302 (m), 1183 (s), 1168 (s), 1151 (s), 1124 (s), 1111 (s), 918 (m), 864 (m), 757 (s), 740 (s), 707 (s), 611 (m), 583 (s), 532 (m), 495 (m); mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) 234 (M^+, 19), 191 (23), 180 (14), 51 (20), 47 (87), 41 (100), 39 (62). At low voltage (10 eV) the molecular ion is the base peak. Uv_{max} (95% EtOH) 272 nm (ε 595), 265 (685), 254 (sh, 317), 220 (10,200).

An analytical sample was prepared by recrystallizing from benzene–hexane and subliming at 150° (0.1 mm), mp 157–159°.

Anal. Calcd for $C_{14}H_{19}OP$: C, 71.76; H, 8.17; P, 13.22. Found: C, 71.84; H, 8.27; P, 13.11.

9-Phenyl-9-phosphabicyclo[4.2.1]nonane Oxide (22) with Phenyllithium. A solution of 100 mg (0.428 mmol) of **22** in 5 ml of dry THF in the apparatus described for phosphonium salt reactions was cooled to −78° and 0.5 ml (1.1 mmol) of phenyllithium added. The mixture was stirred for 5 min and quenched with 1.0 ml of 25% aqueous HBr. After the mixture was warmed to room temperature no solid was present. Ether and water were added, the layers were separated, and the aqueous layer was extracted (2 × 25 ml) with ether and (4 × 20 ml) with chloroform. Both solutions were dried ($MgSO_4$) and stripped. The ether solution afforded only residue from the phenyllithium. The chloroform solution gave 63 mg (63%) of crude **22** as shown by nmr. No salt **24** could be found.[18]

9-Phenyl-9-phosphabicyclo[4.2.1]nonane (23). A 200-ml, three-necked, round-bottomed flask equipped with a nitrogen inlet, reflux condenser, serum cap, stopper, and magnetic stirrer was flamed out with a nitrogen purge. 9-Phenyl-9-phosphabicyclo[4.2.1]nonane oxide (**22**) (2.16 g, 9.24 mmol) was placed in the flask and dissolved in 30 ml of dry benzene. Si_2Cl_6 (2.03 ml, 3.23 g, 12.01 mmol, 30% excess) was injected all at once *via* the serum cap, and the solution was refluxed for 0.5 hr. The stopper was replaced by a pressure-equalizing dropping funnel, and the solution was cooled to 0°. The following manipulations were then conducted under a blanket of nitrogen. Aqueous sodium hydroxide (40 ml, 30%) was added slowly from the dropping funnel, the layers were separated, and the aqueous layer was extracted (3 × 40 ml) with benzene. The combined benzene layers were dried ($MgSO_4$) and stripped. The oily residue crystallized after a few minutes at room temperature and was sublimed at 60° (0.05 mm) giving 1.25 g (62%): mp 58–60°; nmr ($CDCl_3$) 2.78 (m, 4.85 H), 7.12 (doublet of multiplets, $|J_{PH}|$ = 17.0 Hz, 2.00 H, bridgehead), 7.25 to 9.13 (broad m, 12.15 H); ir (KBr) 3060 (w), 3040 (w), 2950 (s), 2830 (s), 1584 (m), 1565 (w), 1477 (s), 1441 (s), 1431 (s), 1361 (w), 1303 (w), 1174 (m), 1127 (w), 1063 (m), 1023 (m), 918 (s), 907 (m), 747 (s), 705 (s), 585 (m), 565 (s), 510 (s); mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) (M + 1, 15), 218 (M^+, 100), 217 (25), 203 (36), 190 (21), 189 (22), 177 (20), 176 (34), 175 (22), 164 (15), 163 (18), 162 (52), 161 (15), 136 (44), 135 (14), 133 (20), 115 (10), 110 (10), 109 (57), 108 (58), 107 (39), 91 (36), 83 (21), 81 (12), 79 (20), 78 (17), 77 (19), 67 (30), 65 (22), 57 (17), 55 (18), 53 (13), 51 (15), 41 (47), 39 (32); uv_{max} (95% EtOH) 260 (ε 7660).

9,9-Diphenylphosphoniabicyclo[4.2.1]nonane Bromide (24a). 9-Phenyl-9-phosphabicyclo[4.2.1]nonane (**23**) (735 mg, 3.37 mmol) was placed in a 10-ml, round-bottomed flask equipped with a reflux condenser and nitrogen inlet, which had been flamed out under nitrogen before use. "Anhydrous" nickel bromide (370 mg, 1.69 mmol), from City Chemical Co., New York (used without purification), was added, and the mixture was melted for *ca.* 5 min at 180° to ensure complex formation. The flask was cooled to room temperature, 0.75 ml (1.07 g, 6.8 mmol) of bromobenzene was added, and the mixture was heated in an oil bath at 180° for 3 hr. (An additional 0.5 ml of bromobenzene was added after 2 hr because the mixture appeared dry.) The dark green mixture was cooled to room temperature and hydrolyzed with 20 ml of water, the green solid giving way to a green solution. The solution was extracted (2 × 20 ml) with ether to remove unreacted starting materials, and then (5 × 20 ml) with chloroform. The combined chloroform layers were dried ($MgSO_4$) and stripped leaving an oily residue, which was crystallized from methanol–ether, washed with ether, and dried at the aspirator giving 1.18 g (94% yield, 89% if the material is a monohydrate) of white crystals, mp 242–244°. When the sample is heated, water is given off at approximately 120°. The entire sample was purified by recrystallizing it twice from methanol between +65 and −78° in a Craig tube and drying it at 140° (0.05 mm) for 2 days: mp 244–246°; nmr ($CDCl_3$) 1.58 (m, 3.78 H, ortho aromatics), 2.48 (m, 5.70 H, meta and para aromatics), 5.25 (m, 1.85 H, bridgeheads), 7.33–9.16 (broad m, 12.65 H); ir (KBr) 3045 (w), 3000 (m), 2910 (s), 2860 (m), 1583 (m), 1445 (s), 1435 (s), 1334 (w), 1301 (w), 1160 (w), 1145 (w), 1115 (s), 1042 (w), 997 (m), 920 (m), 750 (s), 725 (s), 712 (s), 690 (s); uv_{max} (95% EtOH) 274 nm (ε 1610), 267 (2120), 261 (1700), 256 (shoulder, 1200), 233 (19,900).

Anal. Calcd for $C_{20}H_{24}BrP$: C, 64.00; H, 6.45; Br, 21.30; P, 8.25. Found: C, 64.11; H, 6.41; Br, 21.33; P, 8.06.

Reaction of 9,9-Diphenylphosphoniabicyclo[4.2.1]nonane Bromide with Phenyllithium. Ylide 25 and Deuterated Salt 24b. 9,9-Diphenylphosphoniabicyclo[4.2.1]nonane bromide (**24a**) (200 mg, 0.534 mmol) was suspended in 15 ml of anhydrous ether, 1.0 ml of 2.3 *M* (2.3 mmol) phenyllithium solution was added, and the mixture was stirred rapidly. The white solid slowly disappeared, and after 0.5 hr, a yellow solution was present. The mixture was then quenched with 0.2 ml of 48% DBr in D_2O. The color discharged, and a white solid reappeared. After stirring for 5 min, 5 ml of water was added and the mixture was stirred until the salt dissolved. The layers were separated; the aqueous layer was extracted (2 × 10 ml) with ether and then with chloroform (4 × 10 ml). Both extracts were dried ($MgSO_4$) and stripped. The ether solution contained only biphenyl and hydrocarbon material present as impurities in the phenyllithium solution. The chloroform extract gave 197 mg of oil, which was crystallized from methanol–ether. Recrystallization from methanol between +65 and −78° gave, after drying at 140° (0.05 mm), 63 mg (32%) of white crystals, mp 243–245°. The ir spectrum is identical with that of the starting material **24a**. The nmr spectrum is identical with that of the starting material, but the intensity of the resonance at τ 5.25, corresponding to the bridgehead position, is decreased. The ratio of the sum of the intensities of all other resonances and of the resonance at τ 5.25 was 22:0.89. After a similar experiment using THF as the solvent, 0.53 mmol of salt, and 1.1 mmol of C_6H_5Li, the ratio was measured as 22:1.01. After another experiment using THF as solvent, 0.16 mmol of salt, and 0.33 mmol of C_6H_5Li, the ratio was measured as 22:1.07.

Rhodium Catalyzed Isomerization of Methylphosphahomocubane Oxide (10) to 29A and 29B. A 100-ml, round-bottomed flask equipped with a reflux condenser and nitrogen inlet was evacuated and filled with nitrogen four times. Methylphosphahomocubane oxide (**10**) (1.14 g, 6.87 mmol), 150 mg of $[Rh(NBD)Cl]_2$[59] (5 mol %), and 25 ml of chloroform were added and the solution was refluxed under nitrogen. An aliquot was withdrawn periodically and examined by nmr to determine when the reaction was complete. After 18 hr, only one P-CH_3 resonance was observed. The solution was then cooled and stirred with 20 ml of aqueous potassium cyanide for 10 min to destroy the catalyst. The layers were separated, and the aqueous layer was extracted (2 × 20 ml) with chloroform. The chloroform layers were dried ($MgSO_4$) and stripped. The crystalline residue was pumped *in vacuo* to remove traces of norbornadiene, and the residue was then sublimed between 90 and 155° (0.1 mm) giving 906 mg (80%) of white crystals. A melting point determination showed some of the sample melting in a range betwen 64 and 74° and the rest between 110 and 120°. Some of the last material to sublime melted between 113 and 124°. The nmr is described in Table II. In the corresponding phenyl compound, **18**, the resonance of H_2 is at τ 7.10 and in its phosphorus epimer at τ 6.20. By analogy, the resonance of H_2 in **29A** is then probably the one at higher field (τ 6.83) and that of **29B** at lower field (τ 6.32) (see Table II). Integration of these resonances shows the mixture to consist of 59% **29A** and 41% **29B**: ir (1% in CCl_4) 1214.0 cm^{-1} (P–O); mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) 166 (M^+, 31), 165 (76), 133 (18), 105 (14), 104 (100), 103 (66), 102 (12), 79 (12), 78 (~100), 77 (39), 63 (14), 52 (28), 51 (36), 50 (20), 47 (25), 39 (36).

9-Methyl-9-phosphatricyclo[4.2.1.$0^{2,5}$]nonane Oxide (26). A mixture of 2.50 g (15.05 mmol) of **29A** and **29B**, 50 ml of methanol, and 300 mg of platinum oxide was hydrogenated at room temperature and atmospheric pressure; 98% of the theoretical amount of hydrogen was taken up. The catalyst was filtered, and the solution was stripped to leave an oil which slowly crystallized. Sublimation between 45 and 70° (0.05 mm) gave 2.24 g (88%), mp 55–61°: nmr ($CDCl_3$) 6.73 (m), 8.25 (d, $|J_{PH}|$ = 12.5 Hz), 8.42 (d, $|J_{PH}|$ = 12.5 Hz), both doublets superimposed on a broad multiplet ranging from 7.10 to 8.75; mass spectrum (since the base peak was off scale in all spectra, only those peaks with relative intensity ≥20% are listed) *m/e* (rel intensity) 170 (M^+, 100), 169 (23), 155 (27), 142 (60), 129 (29), 116 (36), 115 (25), 104 (40), 91 (50), 90 (22), 80 (51), 79 (95), 78 (40), 77 (38), 67 (20), 63 (25), 54 (37), 53 (23), 47 (20), 41 (39), 39 (34).

(59) R. R. Schrock, Ph.D. Thesis, Harvard University, 1971.

9,9-Dimethyl-9-phosphoniatricyclo[4.2.1.0^{2,5}]nonane Iodide (30). A 200-ml, three-necked, round-bottomed flask equipped with a reflux condenser, nitrogen inlet, serum cap, stopper, and magnetic stirrer was flamed under nitrogen. The mixture (2.15 g, 12.65 mmol) of methylphosphine oxides **26A** and **26B** was placed in the flask, and 50 ml of dry benzene was syringed in. Hexachlorodisilane (4.20 ml, 6.37 g, 25 mmol) was added to the solution by syringe. The resulting cloudy yellow mixture was stirred at room temperature for 30 min and refluxed for 15 min. The clear reddish solution was cooled to 0° and hydrolyzed by adding 50 ml of 30% sodium hydroxide solution in drops from an addition funnel that replaced the stopper. The layers were separated, and the aqueous layer was extracted (3 × 40 ml) with benzene. The benzene solution was dried ($MgSO_4$) and filtered into a 250-ml, round-bottomed flask containing a stirring bar. Methyl iodide (5.0 ml, 80 mmol) was added, and the mixture was stirred for 3.5 hr under nitrogen. The salt was filtered, washed well with benzene and then ether, and sucked dry to give 2.70 g (72%) of crude product, which was recrystallized from absolute ethanol–ether and dried overnight over P_2O_5 at 100° (0.05 mm) giving 2.43 g (65%), mp 304–305° dec. Addition of ether to the mother liquor gave another 70 mg, a 67% total yield: nmr ($CDCl_3$) 7.61 (d, $|J_{PH}|$ = 14.5 Hz), 7.75 (d, $|J_{PH}|$ = 14.5 Hz), superimposed on broad multiplet between 6.55 and 8.22.

An analytical sample was prepared by recrystallizing again from ethanol–ether and drying as above, mp 305° dec.

Anal. Calcd for $C_{10}H_{16}IP$: C, 40.56; H, 6.12; I, 42.86; P, 10.46. Found: C, 40.36; H, 5.95; I, 43.08; P, 10.20.

9,9-Dimethyl-9-phosphoniatricyclo[4.2.1.0^{2,5}]nonane Iodide (30) with Methyllithium 31 and 28. **30** (888 mg, 3.0 mmol) was suspended in 25 ml of anhydrous ether and stirred vigorously while 2.0 ml (3.2 mmol) of methyllithium was added. The mixture was stirred for about 45 min and quenched with 15 ml of water. The aqueous layer was extracted (3 × 20 ml) with ether. The combined ether layers were washed with 15 ml of water, dried ($MgSO_4$), and stripped leaving 38 mg (7%) of a clear oil, which is probably the trimethylphosphorane **31**. The yield ranged between 4 and 12% in eight experiments. The aqueous layer was acidified with HI (until acidic to pH paper) and extracted (5 × 20 ml) with chloroform. The chloroform layers were dried (Na_2CO_3, $MgSO_4$) and stripped leaving 620 mg (66.4%) of white crystalline trimethyl(2-bicyclo[4.2.0]octyl)phosphonium iodide (**28**), identical by ir and nmr with the material obtained below, mp 244–245° dec.

The structure was assigned to **31** primarily on the basis of the nmr spectrum. A P–CH_3 doublet with $|J_{PH}|$ = 8.5 Hz is present at τ 9.00 at 60 MHz and at τ 8.99 at 220 MHz. Impurities appear to be present, however, and the spectrum could not be integrated accurately. (At 220 MHz, doublets at τ 9.08 ($|J|$ = 8.5 Hz), 9.56 ($|J|$ = 12.0 Hz), and 9.85 ($|J|$ = 11.0 Hz) are observed.) The compound is sensitive to air or heat; neat samples or C_6D_6 solutions decompose in a few hours at room temperature and purification was impossible. After storage at −78° under nitrogen, neat or in C_6D_6 solution, no apparent decomposition had taken place after 6 weeks.

A sample was submitted for mass spectrometric analysis. Only when the sample was heated to 150° could a parent peak, *m/e* 184 (15% of the base peak), be observed; this is almost certainly due to a betaine or an ylide formed by cleaving the ring–phosphorus bond. The base peak is *m/e* 76, corresponding to trimethylphosphine, but no peak at *m/e* 108 (1,5-cyclooctadiene) was detected.

Heating a sample in degassed C_6D_6 (sealed at 10^{-6} mm) at 75° resulted in the disapperance of the P–CH_3 doublet in the nmr, but no cyclooctadiene or trimethylphosphine could be detected. Some solid appeared in the sample and may in fact be insoluble betaine.

Dimethyl(2-bicyclo[4.2.0]octyl)phosphine Oxide (27) from 19. **19** (232 mg, 1.0 mmol) was dissolved in 10 ml of dry THF in the apparatus described for reactions of phosphonium salts. The solution was cooled to −78° and 0.62 ml (1.0 mmol) of methyllithium was added. The solution was stirred for 45 min at −78°, quenched with 5 ml of water, and warmed to room temperature. Ether (5 ml) was added, the layers were separated, and the aqueous layer was extracted (2 × 10 ml) with chloroform. The combined organic layers were dried ($MgSO_4$) and stripped leaving 160 mg of solid. Recrystallizing twice from hexane gave 65 mg of solid, mp 106–109°. Sublimation at 90° (0.02 mm) gave 56 mg (30%) of white crystals: mp 114–115°; nmr ($CDCl_3$) 8.60 (d, $|J_{PH}|$ = 12.5 Hz), superimposed on broad multiplet, 7.16–9.17; mass spectrum (30 eV, peaks ≥10% intensity) *m/e* (rel intensity) 186 (30), 159 (70), 158 (27), 145 (10), 143 (10), 118 (55), 108 (10), 105 (25), 92 (40), 79 (98), 78 (100), 67 (12).

From 26A and 26B. A mixture of **26A** and **26B** (85 mg, 0.5 mmol) in 5 ml of dry THF was treated with 0.62 ml (1.0 mmol) of methyllithium at −78° for 45 min. Quenching, extracting, and stripping as above gave 95 mg of solid (93 mg theoretical), which was identical (nmr) with **27** obtained above.

Trimethyl(2-bicyclo[4.2.0]octyl)phosphonium Iodide (28) from Dimethyl(2-bicyclo[4.2.0]octyl)phosphine Oxide (27). A 50-ml three-necked, round-bottomed flask equipped with a serum cap, nitrogen inlet, reflux condenser, stopper, and magnetic stirrer was flamed under a nitrogen purge. Dimethyl(2-bicyclo[4.2.0]octyl)-phosphine oxide (**27**) (238 mg, 1.28 mmol) was placed in the flask and dissolved in 10 ml of dry benzene. Si_2Cl_6 (0.35 ml, 2.08 mmol) was added and the solution was then refluxed for 45 min, cooled to 0°, and hydrolyzed with 10 ml of 30% NaOH. The layers were separated and the aqueous layer was extracted (4 × 10 ml) with benzene. The benzene layers were dried ($MgSO_4$), treated with 1.0 ml of methyl iodide, and stirred under N_2 for 4 hr. Filtration gave 220 mg (55%) of white crystals: mp 255–256° dec; mmp (with the material obtained above) 251–252°; nmr ($CDCl_3$) 7.83 (d, $|J_{PH}|$ = 14.0 Hz), superimposed on a broad multiplet extending from 7.20 to 9.10; ir (KBr, Perkin-Elmer 137) 2950 (s), 1450 (m), 1320 (s), 1310 (s), 1250 (w), 1110 (w), 1070 (m), 1020 (s), 990 (s), 965 (s), 880 (m), 775 (s).

9-Methyl-9-phenyl-9-phosphoniatricyclo[4.2.1.0^{2,5}]nonane Iodide (32). A 100-ml, three-necked, round-bottomed flask equipped with a reflux condenser, nitrogen inlet, serum cap, stopper, and magnetic stirrer was flamed in a nitrogen stream. **19** (1.26 g, 5.43 mmol) was placed in the flask and dissolved in 25 ml of dry benzene. Si_2Cl_6 (1.20 ml 1.91 g, 7.10 mmol) was added, the mixture was stirred and refluxed for 15 min, cooled to 0°, and hydrolyzed with 25 ml of 30% aqueous NaOH. The layers were then separated, and the aqueous layer was extracted (3 × 25 ml) with benzene. The benzene layers were dried ($MgSO_4$), filtered, and treated overnight with stirring with 1.5 ml (24 mmol) of methyl iodide. The resulting solid was filtered and air dried, giving 700 mg (36%) of material. Recrystallization from ethanol–ether gave 318 mg (16%) of slightly yellow crystals: mp 210–212°; nmr ($CDCl_3$) 1.78 and 2.30 (m, 4.85 H), 6.00 (broad s, 1.86 H), 7.46 (d, $|J_{PH}|$ = 14.0 Hz) superimposed on a broad multiplet, 6.92–8.08 (13.30 H total).

Base Hydrolysis of Methiodide 32. **32** (315 mg, 0.88 mmol) was suspended in 3.0 ml of 1 *N* NaOH and stirred at room temperature overnight. No change was apparent, so the mixture was refluxed for 2 hr and then cooled to room temperature. The solution was then extracted (4 × 5 ml) with chloroform, and the extracts were dried ($MgSO_4$) and stripped, leaving 165 mg of clear oil. The nmr spectrum of this oil is complex, showing an aromatic resonance at 2.50 and four different P–CH_3 doublets at 8.25, 8.30, 8.38, and 8.42 (each with $|J_{PH}|$ = 12.5 Hz). The mixture was not separated or characterized further.

Silver Catalyzed Rearrangement of Phenylphosphahomocubane Oxide (9) to Phenylphosphahomocuneane Oxide (33). Phenylphosphahomocubane oxide (**9**) (1.14 g, 5.0 mmol) was dissolved in 50 ml of chloroform and 200 mg (1.02 mmol) of anhydrous silver fluoroborate was added. The mixture was refluxed for 4 days and combined with another 1.14-g run. The combined mixtures were concentrated to 5–10 ml and applied to a 2 × 45 cm silica gel column packed in chloroform. Elution with *ca.* 75 ml of chloroform followed by 5% methanol in benzene (until no more product eluted) gave 2.15 g (95% recovery) of white crystals, which, by nmr analysis, were ≥95% isomerized. (Resonances due to starting material are barely detectable by eye, but integration reveals them.) Recrystallization from methanol using a little Norit gave 1.67 g of white crystals, and concentration of the mother liquor gave another 0.15 g, 1.82 g (80%) total, mp 275–277°. The product was dried overnight over P_2O_5 at room temperature (0.1 mm) before use: nmr ($CDCl_3$) 2.52 (m, 5.12 H), 7.20 (m, 1.82 H), 7.55 (m, 4.11 H); ir (1% in $CHCl_3$–CCl_4) 1213.5 (P–O); mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) 228 (M^+, 55), 227 (34), 163 (27), 149 (14), 105 (12), 104 (100), 103 (48), 102 (10), 85 (14), 79 (11), 78 (66), 77 (65), 52 (20), 51 (58), 50 (20), 49 (13), 47 (33).

An analytical sample was prepared by recrystallizing a portion of the first crop two times from methanol and drying overnight over P_2O_5 at 100° (0.1 mm), mp 278–279° dec.

Anal. Calcd for $C_{14}H_{13}OP$: C, 73.67; H, 5.74; P, 13.57. Found: C, 73.66; H, 5.67; P, 13.45.

Methylphosphahomocuneane Oxide (34). Methylphosphahomocubane oxide (**10**) (1.28 g, 7.71 mmol) was dissolved in 50 ml of chloroform and 500 mg (2.56 mmol) of silver fluoroborate was added. The mixture was refluxed for 5 days, cooled to room

temperature, and concentrated to *ca.* 5 ml. The residue was applied to a 2 × 45 cm silica gel column packed in chloroform and eluted with 200 ml of chloroform followed by 200 ml of 10% methanol in chloroform. Evaporation of the latter eluent left 1.35 g of white crystalline material, mp 160–163°, whose nmr spectrum showed the rearrangement to be complete. Recrystallization from benzene gave 930 mg of white crystals, mp 161–163°. Treatment of the mother liquor with Norit and concentration gave a second crop, 110 mg, mp 161–163°. Both crops were combined and sublimed at 120° (0.05 mm) to give 1.02 g (80%) of product: mp 162–163.5°; nmr ($CDCl_3$) 7.63 (broad s, 6.03 H) and 8.28 (d, $|J_{PH}|$ = 11.5 Hz) superimposed on a multiplet (4.97 H total); ir (1% in CCl_4) 1204.5 (P-O); mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) 167 (M + 1, 11), 166 (M^+, 82), 165 (M − 1, 100), 151 (20), 105 (32), 104 (65), 103 (47), 102 (17), 101 (35), 97 (20), 85 (12), 83 (20), 78 (55), 77 (39), 71 (20), 69 (22), 60 (12), 57 (38), 55 (28), 52 (13), 51 (16), 47 (15), 45 (16), 43 (28) 41 (24), 39 (17).

Phenylphosphahomocuneane Methiodide (35). A 200-ml, three-necked, round-bottomed flask equipped with a N_2 inlet, reflux condenser, serum cap, stopper, and magnetic stirrer was flamed under a N_2 stream. Phenylphosphahomocuneane oxide (**33**) (912 mg, 4.0 mmol) was placed in the flask, and 30 ml of dry benzene was injected through the serum cap. The suspension was stirred rapidly while 0.88 ml (1.40 g, 5.2 mmol) of Si_2Cl_6 was injected all at once. The suspension gave way to a yellow solution, which was refluxed for 20 min and then cooled to 0°. The stopper was replaced with a pressure-equalizing addition funnel, and 20 ml of 30% aqueous NaOH was added (slowly at first because of HCl neutralization). The layers were then separated, and the aqueous layer was extracted (3 × 30 ml) with benzene. The combined benzene layers were dried ($MgSO_4$) and quickly filtered through a sintered glass frit. The clear colorless solution was not concentrated (polymer begins to form if it is), but was treated directly with 2.0 ml (32 mmol) of methyl iodide under N_2 and stirred overnight. (Precipitate appeared almost instantly.) The solid was filtered, washed with benzene, and air dried, giving 1.07 g (76%) of crude methiodide. Two recrystallizations from absolute ethanol followed by drying at 100° (0.1 mm, P_2O_5) gave 935 mg (66%) of material suitable for further use: mp 230–232°; nmr ($CDCl_3$) 1.72 (m, ortho aromatics, 1.91 H), 2.33 (m, meta and para aromatics, 3.11 H), 5.84 (d of m, bridgehead, $|J_{PH}|$ = 9.5 Hz, 1.84 H), 7.33 (d, $|J_{PH}|$ = 14.0 Hz) superimposed on a multiplet (6.80 H total), 7.74 (m, 2.34 H).

Three further recrystallizations from absolute ethanol followed by drying overnight at 100° (0.1 mm, P_2O_5) gave an analytical sample, mp 236–237.5° dec.

Anal. Calcd for $C_{15}H_{16}IP$: C, 50.87; H, 4.55; I, 35.83; P, 8.75. Found: C, 50.76; H, 4.65; I, 35.82; P, 8.58.

Dimethylphosphoniahomocuneane Iodide (36). A 100-ml, three-necked, round-bottomed flask equipped with a N_2 inlet, reflux condenser, serum cap, stopper, and magnetic stirrer was flamed under nitrogen. Methylphosphahomocuneane oxide (**34**) (664 mg, 4.0 mmol) was added and dissolved in 20 ml of dry benzene. Si_2Cl_6 (0.925 ml, 1.48 g, 5.50 mmol) was injected through the serum cap, and the solution was refluxed for 15 min. The solution was cooled to 0°, the stopper replaced with a pressure-equalizing addition funnel containing 20 ml of 30% aqueous sodium hydroxide, and the sodium hydroxide solution was added to the benzene solution slowly with rapid stirring. The resulting two layers were separated, and the aqueous layer was extracted (3 × 20 ml) with benzene. The combined benzene layers were dried ($MgSO_4$) and filtered. Methyl iodide (1.0 ml, 16 mmol) was added to the filtrate, and the solution was stirred under N_2. Precipitation of the salt began almost immediately. After 7 hr, the solid was filtered, washed with benzene, and air dried, giving 1.13 g of crude methiodide. Recrystallization from absolute ethanol (Norit) gave 975 mg of off-white crystals, mp 257–260° dec. A second recrystallization from absolute ethanol gave, after drying at 100° (0.05 mm, P_2O_5, overnight), 888 mg (76%) of white crystals: mp 259–260° dec; nmr ($CDCl_3$–CD_3OD) 6.52 (d of m, $|J_{PH}|$ = 10.0 Hz, bridgehead, 2.19 H), 7.67 (d, $|J_{PH}|$ = 13.5 Hz), superimposed on a multiplet (11.81 H total).

Phenylphosphahomocuneane Methiodide (35) with Phenyllithium Semibullvalene. In Diethyl Ether. Phenylphosphahomocuneane methiodide (**35**) (177 mg, 0.5 mmol) was suspended in 5 ml of ether, 0.25 ml (0.58 mmol) of phenyllithium solution was added, and the yellow mixture was stirred vigorously for 0.5 hr. All solids dissolved after 5 min. The solution was quenched with 5 ml of water, and the layers were separated. The aqueous layer was extracted (3 × 10 ml) with ether and the combined organic layers were dried ($MgSO_4$) and stripped at 0°, leaving 124 mg of crude material. Distillation at 1 × 10^{-5} mm (rt to −196°) gave 37 mg of foul-smelling pale yellow oil. The nmr spectrum showed only benzene and semibullvalene[25] in the ratio of 23:77, as estimated from the integration, which represents an absolute yield of 58% of semibullvalene. Nmr analysis of the mixture before distillation showed the presence of diphenylmethylphosphine (which did not distill under these conditions), identified by its methyl doublet: found ($CDCl_3$) 8.42 ($|J_{PH}|$ = 3.5 Hz); found for an authentic sample ($CDCl_3$) 8.45 ($|J_{PH}|$ = 3.5 Hz);[60] reported (neat) 8.49 ($|J_{PH}|$ = 6.0 Hz).[61]

In Diethyl Ether with Internal Standard. A similar experiment was performed using 2.0 ml of 0.45 *M* (0.9 mmol) phenyllithium in ether[30] and 177 mg (0.5 mmol) of salt **35**. The ether layer obtained on extraction was dried ($MgSO_4$) and concentrated by distillation through a short Vigreux column at atmospheric pressure until no more ether distilled. The high vacuum distillation was then carried out as before on the residue. CH_2Cl_2 (31.8 μl, 0.500 mmol) was then added to the clear distillate and the nmr spectrum determined in CCl_4. Repeated (5×) integration of the low-field multiplet of semibullvalene (2 H) and the singlet of CH_2Cl_2 showed the yield of semibullvalene to be 56%.

With Phenyllithium in Dimethyl Ether. The same apparatus was used, except that the stopper was replaced with a small Dry Ice condenser. Phenyllithium (2.2 ml, 0.45 *M*, 1.0 mmol) in ether[30] was injected into the flask and the ether was removed with a vacuum pump and then nitrogen admitted. Salt **35** (177 mg, 0.5 mmol) was added quickly to the solid phenyllithium against a stream of nitrogen flowing from the flask. The flask was cooled to −78° and 25 ml of dimethyl ether was distilled into it from $LiAlH_4$. The resulting mixture was then stirred for 0.5 hr at −78°, warmed to the point of reflux, and the solvent concentrated to about 10 ml through a short column. The mixture was then allowed to reflux for 1 hr. The condenser was removed and the solvent distilled at atmospheric pressure through a short Vigreux column into a trap at −78°. The residue was then distilled at room temperature (0.5 mm) into a trap at −196°, giving 33 mg of colorless oil. The nmr spectrum showed the oil to be 62% semibullvalene and 38% benzene, thus representing a 45% yield of semibullvalene. The ir spectrum also showed the characteristic absorptions of semibullvalene.[25]

With Methyllithium in Diethyl Ether. Salt **35** (89 mg, 0.25 mmol) in 3 ml of diethyl ether was treated with 0.18 ml (0.29 mmol) of methyllithium. The salt disappeared instantly and a yellow color developed. After 15 min, hydrolysis and work-up as above (no distillation of the residue) gave 20 mg of crude semibullvalene and dimethylphenylphosphine, plus a small trace of dimethylphenylphosphine oxide, all identified by the nmr spectrum of the crude reaction mixture. For dimethylphenylphosphine: found ($CDCl_3$) 8.70 (d, $|J_{PH}|$ = 2.5 Hz); found for an authentic sample,[60] 8.67 (d, $|J_{PH}|$ = 2.3 Hz); reported,[62] ($CDCl_3$) 8.61 (d, $|J_{PH}|$ = 1.7 Hz). For dimethylphenylphosphine oxide: found ($CDCl_3$) 8.27 (d, $|J_{PH}|$ = 13.0 Hz); reported[63] ($CDCl_3$) 8.22 (d, $|J_{PH}|$ = 13.0 Hz).

With Methyllithium in Dimethyl Ether. The same apparatus and procedure were used as for the previous experiment using $(CH_3)_2O$. Methyllithium (1.5 ml, 2.4 mmol) and 177 mg (0.5 mmol) of **35** were used. Work-up as before [solvent removal was with a warm (35°) water bath] gave 19 mg of semibullvalene contaminated with dimethylphenylphosphine as shown by nmr. The nmr sample (CCl_4) turns cloudy and polymerizes on standing.

Dimethylphosphoniahomocuneane Iodide (36) with Methyllithium. Dimethylphosphoniahomocuneane iodide (**36**) (292 mg, 1.0 mmol) was suspended in 10 ml of ether. The suspension was stirred rapidly, and 1.0 ml (1.6 mmol) of methyllithium in ether was added all at once through the serum cap. The salt disappeared in 20 min, and after 30 min total reaction time, the mixture was quenched with 5 ml of H_2O. (Gas was evolved and a strong phosphine odor was detected.) The layers were separated, and the aqueous layer was extracted (2 × 5 ml) with ether. The combined ether layers were dried ($MgSO_4$) and concentrated at atmospheric pressure to about 1 ml through a short Vigreux column. The pot was cooled, and 44.5 μl (0.50 mmole) of C_6H_6 was added. The nmr spectrum of the ether solution was then determined; it showed only resonances due to semibullvalene, benzene, and ether. (Another run in which

(60) Sample obtained from J. Mayerle.
(61) M. J. Gallagher, *Aust. J. Chem.*, 1197 (1968).
(62) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).
(63) P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967).

the ether was stripped at room temperature also showed only semibullvalene.). Integration (average of seven scans) of the low-field semibullvalene multiplet resonance and the benzene resonance showed the yield of semibullvalene to be 69%. The nmr sample, the remainder of the pot, and the distillate were combined and treated with excess methyl iodide in ether, giving tetramethylphosphonium iodide, which was filtered, washed with ether, and sucked dry. The yield was 77 mg (35%). Its nmr spectrum in DMSO-d_6 shows only a doublet at τ 8.09, $|J_{PH}|$ = 15.0 Hz; lit.[64] spectrum in DMSO-d_6, τ 8.08, $|J_{PH}|$ = 14.8 Hz; mp >315° (lit.[26] mp > 360°) (impure product melts 312–322° dec[26]).

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene Methiodide (40) with Phenyllithium. **40** (354 mg, 1.0 mmol) was suspended in 10 ml of ether and 0.5 ml of 2.3 *M* (1.15 mmol) phenyllithium was added. The mixture was stirred for 3 hr at room temperature and quenched with 5 ml of water. A lot of polymeric material was present. The layers were separated, and the aqueous layer was extracted (3 × 10 ml) with ether. The combined ether layers were dried ($MgSO_4$) and concentrated to about 0.5 ml by distillation at atmospheric pressure through a short Vigreux column. The residue was then distilled, room temperature to −196° (10^{-6} mm), to give a pale yellow ethereal solution. CH_2Cl_2 (31.8 μl, 0.50 mmol) was added, and the nmr spectrum was determined. Five integrations of the COT resonance at τ 4.33 and the CH_2Cl_2 resonance showed the yield of COT to be 31%. The nmr spectrum of the pot (C_6D_6) indicated the presence of impure diphenylmethylphosphine, identified by the chemical shift and coupling constant of the methyl doublet. Found, τ 8.61, (d, $|J_{PH}|$ = 4.0 Hz); found for an authentic sample[60] (C_6D_6) τ 8.60 (d, $|J_{PH}|$ = 4.0 Hz).

1,1-Diphenylphospholanium Bromide (42a). 1-Phenylphospholane[65] (2.03 g, 12.4 mmol) was placed in a dry 50-ml, round-bottomed flask equipped with a reflux condenser and nitrogen inlet. Anhydrous $CoCl_2$[21] (800 mg, 6.20 mmol) was added and a brown complex formed instantly. Bromobenzene (2.60 ml, 3.90 g, 24.8 mmol) was added all at once and the resulting blue mixture heated in a bath at 200° for 3 hr. The mixture was then cooled and hydrolyzed with 20 ml of water. When the blue solid had disappeared and a pink solution was present, the solution was extracted (2 × 20 ml) with ether and (5 × 20 ml) with chloroform. The chloroform layers were dried ($MgSO_4$) and stripped, leaving an oily residue which crystallized from acetone on cooling overnight in the freezer. Filtration, washing with acetone, and drying at 100° (0.05 mm, P_2O_5, 3 hr) gave 2.19 g. Concentration of the mother liquor gave, after drying, another 356 mg, a total yield of 2.55 g (64%): mp 164–166° (lit.[27] mp 162°); nmr ($CDCl_3$) 2.00 and 2.28 (m, 9.86 H), 6.75 (m, 3.80 H), 7.62 (m, 4.34 H).

1,1-Diphenylphospholanium Bromide (42a) with Phenyllithium. 1,1-Diphenylphospholanium bromide (**42a**) (500 mg, 1.56 mmol) suspended in 10 ml of THF was stirred rapidly while 0.71 ml of 2.2 *M* (1.56 mmol) phenyllithium was added. A reddish-brown solution developed within 5 min, and after stirring for 15 min was quenched with 0.2 ml of 48% DBr in D_2O. The color discharged instantly. Water (5 ml) and ether (5 ml) were added, and the layers were separated. The aqueous layer was extracted (2 × 10 ml) with ether and (5 × 10 ml) with chloroform. The chloroform solution was dried ($MgSO_4$) and stripped, giving a quantitative recovery of salt, which crystallized from acetone overnight in the freezer. Filtration and drying at 100° (0.05 mm) for 3 hr gave 227 mg (45%) of pure salt **42b**, mp 161–163°. Its nmr spectrum showed the intensity of the resonance at τ 6.75 to be 2.67 compared with 10.00 for the aromatic resonance. In the protiated compound **42a** this value is 3.83. These results show that one atom of deuterium is present in **42b**.

Rate of Hydrogen–Deuterium Exchange of Dimethylphosphoniahomocubane Iodide (8) in NaOD. Sodium deuteroxide solution, prepared by slowly adding pieces of sodium to D_2O, titrated (phenolpthalein) as 0.27 *M*. Dimethylphosphoniahomocubane iodide (**8**, 349 mg, 1.195 mmol) was placed in a 5-ml volumetric flask. The flask and a bottle containing the NaOD solution were placed in a bath thermostated at 26.8°. After 1 hr, 4.0 ml of NaOD solution was transferred to the volumetric flask, which was quickly shaken to dissolve the salt and returned to the bath. This afforded a solution 0.299 *M* in phosphonium salt and 0.27 *M* in NaOD. An aliquot (*ca.* 0.5 ml) was withdrawn every half-hour and quenched with excess HI. Stripping left a solid, which was washed three times with acetone (to remove NaI) and dried by pumping. The proton nmr spectrum was then determined in $CDCl_3$. The ratio of the intensities of the methyl and cage resonances was determined by averaging three integrations. (The bridgehead hydrogens were assumed not to exchange on the basis of experiments described below using 1 *N* LiOD.) The ratio at zero time was assumed to be 0.75. The ^-OD titer determined by titrating the last aliquot was 0.25 *M*.

The following data points were obtained: time, min (*r*, ratio of methyl and cage proton nmr intensities) 0.0 (0.750), 30.2 (0.630), 60.4 (0.579), 90.3 (0.556), 119.9 (0.448), 150.2 (0.450), 180.0 (0.392), 250.3 (0.299).

Log (400*r*/3) appears linear in time and the pseudo-first-order rate constant determined from the slope that fits the data best using the method of least squares is (5.84 ± 0.22) × 10^{-5} sec^{-1}. The error is the "probable error" of the least-squares fit.

Deuterium Exchange of Dimethylphosphoniahomocubane Iodide (8) at Room Temperature. Dimethylphosphoniahomocubane iodide (**8**, 100 mg, 0.342 mmol) was dissolved in 1.0 ml of 1 *N* LiOD (prepared by slowly adding 7 mg of lithium powder containing 1% sodium to 1.0 ml of deuterium oxide) and the solution was stirred for 13 hr. Extraction with chloroform (4 × 2 ml), drying ($MgSO_4$), and stripping left 132 mg. The nmr spectrum of this deuterated substance is described in the text. This deuterated material (70 mg) was stirred with 1 *N* LiOD-D_2O for 1 week. Work-up as above gave 58 mg of salt. The nmr spectrum again showed that no exchange had occurred at the bridgehead (see the text). Treating 100 mg of **8** with 10 mg of Na_2CO_3 in 1.0 ml of D_2O for 6 hr at room temperature incorporated no deuterium into the molecule.

At 100°. Dimethylphosphoniahomocubane iodide (**8**) (75 mg, 0.256 mmol) was dissolved in 0.75 ml of 1 *N* LiOD (prepared as above) and sealed in a bomb tube at 0.05 mm. The tube was kept in an oil bath thermostated at 100° for 6 days. The tube was cooled to room temperature, opened, and the contents was extracted (4 × 2 ml) with chloroform. The chloroform extracts were dried ($MgSO_4$) and stripped, leaving 105 mg of white solid. The nmr of this material is also described in the text.

Attempted Exchange of Salt 2 at 100°. Diphenylphosphoniahomocubane bromide (**2**) (117 mg, 0.317 mmol) was suspended in 0.75 ml of 1 *N* LiOD and sealed in a bomb tube at 0.06 mm. The tube was placed in an oil bath thermostated at 100° for 20 hr. After cooling to room temperature the tube was opened and was found to smell of benzene. A light yellow oily layer was present on top of the aqueous solution. The entire mixture was extracted (3 × 2 ml) with chloroform, dried ($MgSO_4$), and stripped, leaving 82 mg of white solid (72 mg theor) whose nmr spectrum was identical with that of phenylphosphahomocubane oxide (**9**). No incorporation of deuterium at the bridgehead could be detected in the nmr spectrum.

Thermolysis of the Phosphoranes in Solution. General. Solutions of *ca.* 30–50 mg of each of the phosphoranes in *ca.* 0.3 ml of C_6D_6 were prepared. TMS and 2–3 drops of internal standard were added (toluene was used for **3**, **4**, and **5**, while cyclohexane was used for **6** and anisole for **21**). The solutions were then degassed five times (freeze–pump–thaw) and sealed at 10^{-6} mm in nmr tubes. The nmr spectrum of each sample was then determined and the ratio measured of the intensities of all the ring resonances of each phosphorane and of the internal standard. The samples were then placed in an oil bath thermostated at 75°. (**3** was also heated at 60°.) The nmr spectrum of each sample was measured periodically at ambient temperature to show how much phosphorane was present. Each phosphorane gave a diene and a tertiary phosphine, both of which were detectable by nmr. Table III summarizes the results obtained from these thermolyses. A plot of log (% phosphorane) *vs.* time was linear, and the half-lives in Table III were calculated from the slopes of these plots. Compound **5** darkened extensively after some time, and the plot was linear for only 1 half-life. The other plots were linear for 2 half-lives.

Thermolysis of Phosphorane 3 in the Absence of Solvent. **3** (50 mg, 0.137 mmol) was placed in one bulb of a two-bulb bulb-to-bulb distillation apparatus, which was then sealed at 0.1 mm. The lower bulb, containing solid **3**, was immersed in an oil bath main-

(64) H. H. Sisler and S. R. Jain, *Inorg. Chem.*, 7, 104 (1968).

(65) Prepared by hydrogenating 1-phenylphospholene 1-oxide[66] (PtO_2, CH_3OH, atmospheric pressure, 89%) to 1-phenylphospholane and reducing the phosphorus–oxygen bond with Si_2Cl_6 [75%; bp 85–88° (0.13 mm); lit.[67] bp 125° (14 mm)]. The ir spectrum was identical with that reported.[67]

(66) W. B. McCormack, U. S. Patent 2,663,739; *Chem. Abstr.*, **49**, 7602f (1955); *cf.* W. B. McCormack, *Org. Syn.*, **43**, 73 (1963).

(67) J. H. Davies, J. D. Downer, and P. Kirby, *J. Chem. Soc. C*, 245 (1966).

tained at 120° and the upper bulb was cooled with Dry Ice. Heating was maintained for 10 min, after which time the oil bath was removed, the apparatus was cooled, and the bulbs were broken apart. The nmr spectrum of the volatile material, 12 mg (85%) from the bulb cooled at −78°, showed resonances due only to COT (**14**) and tricyclooctadiene (**43**) in the ratio of 1:4 (by integration). The nonvolatile material (37 mg) in the other bulb was identified by nmr as triphenylphosphine, contaminated with traces of starting material. Recrystallization from methanol gave white crystals, mp 76–77.5°, mmp (with pure triphenylphosphine) 77–78°, whose ir was identical with that of authentic triphenylphosphine.

Thermolysis of Phosphorane 21 in the Absence of Solvent. Phosphorane **21** (37 mg, 0.10 mmol) was sealed in a two-bulb bulb-to-bulb distillation apparatus at 0.1 mm. The upper bulb was cooled with Dry Ice, while the lower bulb, containing the solid phosphorane, was heated for 5 min in an oil bath at 125°. The bath was then removed, the apparatus was cooled, and the bulbs were broken apart. The upper bulb was found to contain 10 mg (94%) of 1,5-cyclooctadiene (**44**) as the only volatile material. The identification was by ir and nmr spectra, both of which were identical with those of authentic material. The lower bulb contained 27 mg (quantitative yield) of off-white crystals, which were recrystallized from methanol and shown to be triphenylphosphine by ir and melting point (80–82°).

Half-Life of Tricyclooctadiene (43). A C_6D_6 solution of **43** containing a drop of toluene was degassed twice, sealed at 0.05 mm in an nmr tube, and placed in an oil bath maintained at 75° by a thermostat. Periodic examination of the sample by nmr showed smooth conversion to COT (**14**), and the half-life was estimated, using nmr integration for analysis, as 7.5 hr.

Photolysis of Phosphorane 3. In C_6D_6. A solution of 22 mg of **3** in 0.3 ml of C_6D_6 containing 16 mg of toluene as internal standard was irradiated through a Pyrex filter at room temperature with a 450-W medium-pressure Hanovia lamp. Periodic analysis by nmr showed the formation of tricyclooctadiene (**43**) but not COT. After 6 hr, 48% of **3** had disappeared. Continued photolysis did not improve the yield.

In CH_2Cl_2. A solution of 200 mg (0.546 mmol) of **3** in 6 ml of CH_2Cl_2 in a Pyrex test tube was photolyzed through a Pyrex filter with a 450-W medium-pressure Hanovia lamp for 6 hr. The CH_2Cl_2 was distilled through a short Vigreux column, and the residue was applied to a column of 10 g of silica gel packed in pentane. The column was eluted with *ca.* 50 ml of pentane and the majority of the pentane was removed by distillation through a short Vigreux column. Pure tricyclooctadiene (**43**) was then isolated by preparative glpc of this residue: column: 10 ft × 0.25 in. 20% Carbowax on 60–30 Chromosorb W; column temperature 50°; injector, collector and detector 60°; flow rate 100 ml of He/min; yield, 8 mg (15% based on starting **3**).

Photolysis of Homocubyltrimethylphosphorane (6). A solution of 20–25 mg of homocubyltrimethylphosphorane **6** in *ca.* 0.3 ml of C_6D_6 containing 2 drops of C_6D_6 as internal standard was irradiated through a Pyrex filter at room temperature with a 450-W medium-pressure Hanovia lamp. Analysis of the solution periodically by nmr showed the presence of tricyclooctadiene (**43**) and trimethylphosphine. After about 7 hr, polymer began to appear. The yield of diene was about 18% after 7 hr, 32% after 27.5 hr, and 37% after 51 hr.

(7-Cycloheptatrienyl)methyldiphenylphosphine Oxide (46) from 49. A 50-ml, three-necked, round-bottomed flask equipped with a serum cap, nitrogen inlet, stopper, and magnetic stirrer was flamed while purging with nitrogen. **49**[13] (400 mg, 1.76 mmol) was placed in the flask and 25 ml of dry THF was syringed in. The solution was cooled to −78° and with stirring, 0.80 ml of 2.2 *M* (1.76 mmol) phenyllithium was added through the serum cap. A reddish-brown color developed instantly. The solution was stirred 5 min at −78° and hydrolyzed with 2.0 ml of 15% aqueous HBr. The color discharged instantly. The mixture was thawed, ether (10 ml) and water (10 ml) were added, and the aqueous layer was extracted (3 × 15 ml) with ether. The combined organic layers were dried ($MgSO_4$) and stripped, leaving an oil, which was chromatographed on 2 × 30 cm silica gel, eluting with 100 ml of pentane and then 300 ml of ether. The uv absorption of the eluents was monitored. The product began to elute in the last 50 ml of ether and was eluted further with 250 ml of 1:1 chloroform–ether. After stripping, 530 mg of solid was obtained, and sublimation at 110° (0.1 mm) gave 318 mg (60%) of pure product: nmr ($CDCl_3$) 2.53 (10.45 H), 3.45 (t, 1.83 H), 3.93 (d of t, 1.89 H), 4.75 (q, 1.89 H), 7.33 (m, 2.97 H). The olefinic region of the spectrum is very similar in line shape to that reported for cycloheptatriene[66] and its 7-substituted derivatives.[66,69] Ir (KBr) 3075 (w), 3056 (w), 3009 (m), 2932 (w), 2855 (w), 1463 (m), 1435 (s), 1395 (m), 1310 (m), 1227 (m), 1181 (s), 1138 (s), 1118 (s), 1102 (m), 1000 (w), 823 (m), 805 (m), 755 (s), 723 (s), 695 (s), 548 (s), 520 (s); mass spectrum (peaks ≥10% intensity) *m/e* (rel tensity) 306 (M^+, 15), 305 (64), 203 (10), 202 (80), 201 (53), 183 (11), 155 (30), 125 (15), 105 (79), 104 (100), 103 (11), 91 (50), 78 (20), 77 (40), 51 (15), 47 (19); uv_{max} (95% EtOH) 303 nm (plateau, ε 6220), 272 (12,220) 218 (sh, 31,600).

An analytical sample was prepared by recrystallizing from cyclohexane–benzene (3:1) and subliming at 110° (0.1 mm), mp 112–113°.

Anal. Calcd for $C_{20}H_{19}OP$: C, 78.41; H, 6.25; P, 10.11. Found: C, 78.46; H, 6.38; P, 10.18.

This material was identical with that prepared directly below (ir, nmr).

(7-Cycloheptatrienyl)methyldiphenylphosphine Oxide (46) from Methyldiphenylphosphine Oxide. A 50-ml three-necked, round-bottomed flask equipped with a reflux condenser, stopper, serum cap, nitrogen inlet, and magnetic stirrer was flamed while purging with nitrogen. A solution of 1.00 g (4.63 mmol) of methyldiphenylphosphine oxide[70] in 25 ml of benzene was stirred while 3.0 ml (4.80 mmol) of 1.6 *M* *n*-butyllithium in hexane[71] was added in one portion through the serum cap. The resulting yellow solution was stirred and refluxed for 3.25 hr. After cooling to room temperature 825 mg (4.63 mmol) of tropylium fluoroborate[72] was added, and the brown mixture was stirred at room temperature for 2 hr. Hydrolysis with 10 ml of water discharged the brown color, and a yellow organic layer formed. The aqueous layer was extracted (3 × 20 ml) with chloroform. The combined organic layers were dried ($MgSO_4$) and stripped, leaving a yellow oil, which was applied to a 2 × 30 cm silica gel column and eluted with ether. The uv absorption of the eluents was monitored. After a forerun of *ca.* 125 ml, the product eluted in the next 300 ml. (Methyldiphenylphosphine oxide was eluted with 1:1 ether–chloroform.) The ether fractions were stripped leaving 400 mg of oil, which solidified on standing and was sublimed at 110° (0.1 mm), giving 155 mg (11%). Recrystallization from benzene–cyclohexane (1:3) gave pure product. The material was identical (ir, nmr) with that obtained directly above.

Phenylphosphahomocuneane Oxide (33) with Phenyllithium. 47. A 50-ml, three-necked, round-bottomed flask equipped with a nitrogen inlet, serum cap, stopper, and magnetic stirrer was flamed and purged with nitrogen. Oxide **33** (228 mg, 1.0 mmol) and 10 ml of ether were added. The suspension was cooled to −78° and stirred with 3.0 ml (1.35 mmol) of phenyllithium in ether.[30] After 5 min at −78°, and 0.5 hr at room temperature, 1.0 ml of 24% aqueous HBr was added and then 5 ml of water. The aqueous layer was extracted (3 × 10 ml) with chloroform and the combined organic layers were dried ($MgSO_4$) and stripped, leaving 185 mg (60%) of crude **47**, which was applied to a 2 × 30 cm silica gel column. The uv absorption of the eluents was monitored (ISCO monitor). Hexane and ether eluted *ca.* 50 mg of hydrocarbon impurity, and 1:1 chloroform–ether eluted 102 mg of yellow oil, which slowly crystallized. Recrystallization from ether and then acetone–hexane and sublimation at 95° (0.05 mm) gave 35 mg (11.5%) of pure **47**: mp 100–101.5° (lit.[32] mp 102–103°); nmr identical with that reported[32] ($CDCl_3$) 2.00–2.65 (m, 10.40 H), 2.80 (s, 4.88 H), 6.80–7.70 (m, 3.72 H); ir (KBr) 3053 (w), 3022 (w), 2930 (w), 1603 (m), 1588 (w), 1496 (s), 1484 (m), 1455 (s), 1438 (s), 1330 (w), 1215 (w), 1178 (s), with shoulders at 1189 and 1164, 1142 (w), 1120 (s), 1103 (m), 1074 (m), 1021 (w), 934 (w), 829 (w), 778 (s), 760 (s), 750 (s), 739 (s), 719 (s), 701 (s), 588 (s). Peaks at 3053, 3022, 1455, and 1142 were not reported previously[32] while those at 1640, 1270, 990, and 860 were, but are missing here. Mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) 306 (M^+,

(68) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3896 (1965).

(69) (a) S. J. Weininger, private communication, Worcester Polytechnic Institute, Worcester, Mass.; (b) H. Günther, M. Görlitz, and H. H. Hinricks, *Tetrahedron*, **24**, 5665 (1968).

(70) Prepared in 80% yield by hydrolyzing methyltriphenylphosphonium iodide in aqueous sodium hydroxide at 100°, mp 112–113°, lit.[63] mp 109–110°. The nmr spectrum was identical with that reported.[63]

(71) From Foote Mineral Co., Exton, Pa.

(72) *Org. Syn.*, **43**, 101 (1963), recrystallized from acetonitrile before use.

15), 203 (13), 202 (100), 201 (15), 155 (16), 125 (12), 91 (77), 78 (20), 47 (14).

With Phenyllithium in 70:30 Benzene–Ether. 46. The reaction described above was conducted with 1.0 mmol of **33** and 1.03 mmol of commercial phenyllithium. The nmr spectrum of the crude reaction product obtained in 66% yield showed besides a singlet at τ 2.80 attributable to **47** only resonances due to **46** and hydrocarbon impurity from the commercial phenyllithium. This mixture was not further characterized.

Phenylphosphahomocuneane Oxide (33) with Methyllithium. 48. A 50-ml, three-necked, round-bottomed flask equipped with a nitrogen inlet, serum cap, stopper, and magnetic stirrer was flamed while purging with nitrogen. Phenylphosphahomocuneane oxide (**33**) (114 mg, 0.50 mmol) and 5 ml of anhydrous ether were added. While stirring the suspension rapidly, 0.5 ml (1.1 mmol) of methyllithium[73] in ether was added through the serum cap. The solid gave way to a yellow solution within 5 min. After 4 hr the reaction was quenched with 5 ml of H_2O, whereupon the yellow color discharged and gas evolved. The aqueous layer was extracted (3 × 10 ml) with chloroform and the combined organic layers were dried ($MgSO_4$) and stripped, leaving 140 mg of off-white crystalline material. Recrystallization from hexane and sublimation at 95° (0.05 mm) gave 80 mg (66%) of white crystals: mp 108–110°; mass spectrum (peaks ≥10% intensity) *m/e* (rel intensity) 244 (M^+, 17), 243 (25), 166 (47), 165 (60), 141 (10), 140 (100), 139 (20), 125 (53), 105 (10), 104 (12), 103 (11), 91 (10), 79 (10), 78 (19), 77 (36), 51 (13), 47 (20).

(73) This methyllithium was in ether solution and contained LiBr. It was obtained from Alfa Inorganics, Beverly, Mass.

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cis[4]-Cyclononatetraeneiron Tricarbonyl. Its Synthesis, Thermal Rearrangement, and Low-Temperature Protonation[1]

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Abstract: The preparation and characterization of *cis*[4]-cyclononatetraeneiron tricarbonyl (III) are reported. This complex is prepared from the reaction of *cis*-bicyclo[6.1.0]nonatriene either photochemically with iron pentacarbonyl or thermally with diiron nonacarbonyl. Additional complexes isolated and characterized from these reactions include *cis*-8,9-dihydroindeneiron tricarbonyl (IV), bicyclo[6.1.0]nonatrieneiron tricarbonyl (V), and the binuclear complex bicyclo[6.1.0]nonatrienediiron hexacarbonyl (VI). The *cis*[4]-cyclononatetraeneiron tricarbonyl complex is stable for days at room temperature but at 101° undergoes electrocyclic ring closure to *cis*-dihydroindeneiron tricarbonyl (IV). The first-order rate constant for this process at 101° is 2.4×10^{-4} sec^{-1} corresponding to $\Delta F^{\ddagger}$ = 28.4 kcal/mol. This is contrasted to the ring closure of *cis*[4]-cyclononatetraene which occurs at 23° with a half-life of *ca.* 50 min ($\Delta F^{\ddagger}$ *ca.* 23 kcal/mol). Low-temperature protonation of cyclononatetraene complex III in FSO_3H–SO_2ClF is observed to occur at C_6 to yield the monocyclic cation X.

Over the past several years the chemistry of diene iron tricarbonyl complexes has received considerable attention and has proved to be interesting and varied. For the organic chemist, one valuable function of the iron tricarbonyl group has been to allow isolation of reactive polyolefins which are not normally stable at room temperature as their metal complexes. Among prominent examples of this phenomenon are cyclobutadieneiron tricarbonyl,[2] cyclopentadienoneiron tricarbonyl,[3] and norbornadien-7-oneiron tricarbonyl.[4]

A second aspect of the chemistry of iron diene complexes in which we have recently been interested is the thermal rearrangements of the bound organic ligands and the comparison of their thermal chemistry with the thermal chemistry of the uncomplexed organic systems. In this regard, we have recently reported the electrocyclic ring closure of 1,3,5-cyclooctatrieneiron tricarbonyl to bicyclo[4.2.0]octadieneiron tricarbonyl,[5] the ring closure of the cyclooctatrienyliron tricarbonyl cation to the bicyclo[5.1.0]octadienyliron tricarbonyl cation,[6] and the thermal conversion of bicyclo[5.1.0]-octadieneiron tricarbonyl to bicyclo[4.2.0]octadieneiron tricarbonyl.[5a]

Interesting from both perspectives is the iron tricarbonyl complex of *cis*[4]-cyclononatetraene (I). Although this tetraene has been prepared at low temperatures by several groups,[7-10] it is unstable relative to its

(1) Research supported by the National Science Foundation (Grant GP-29580) and the North Carolina Board of Science and Technology.

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